

Delft University of Technology

Faculty of Mechanical, Maritime and Materials engineering

Thesis

Identification of the cement type at the concrete surface with ordinary Portland cement and supplementary cementitious materials with a handheld X-ray Fluorescence analyser

Committee:

Dr. M.(Marija) Nedeljković Dr. O.(Oğuzhan) Çopuroğlu Dr.ir. MJM.(Marcel) Hermans Dr.M. (Mohammad) Fotouhi Student:

Jacques Aoustin

ACADEMIC YEAR 2022/2023

Acknowledgement

While looking for a quote, I found the following quote "see, life is a journey and every chapter is very interesting" by Zeenat Aman. This quote particularly resonated with me because of the saying and the person who said it. Tu delft and the Netherlands opened my mind to people from different horizons and countries. I met amazing people in Delft, and I will never thank them enough for their support and help during my time here.

My first thought goes to Julia, who appears to be the person I go to when I have troubles. I would not have guessed we would become such good friends based on our first meeting in the library at 10 pm during covid crisis, followed by numerous study sessions where we would not stop talking and laughing. You are someone central to me, and you helped me figure out who I truly was during this time in Delft. I love your energy and unusual ideas, as when we went to the ecstatic dance or the alternative parties in Berlin and Munich. I am lucky to have met you, and I hope we will continue sharing memorable times. Thanks to you, I also met two other important people: Joanna and Aditya (without an h).

Thanks, Joanna, for your wisdom and calm. You inspire me with your capacity to understand situations. You provide valuable advice when needed, lean an ear under challenging times, and know how to have fun, as for your birthday in Amsterdam. I keep many memories from your too-short era in Delft, such as your birthday in Kampveld, the costume party for Julia's birthday, or the trip to Munich and Paris. I hope to see you this summer!

I feel like I'm saying the same thing about everyone, but the first word which comes to my mind when I think of you is kindness. You are someone I also feel close by the time we shared and the quality of our interaction. Thank you for all those evenings spent discussing existential questions.

Thank you to all my past and present roommates at 107 Oude Delft. Living with roommates is not always the easiest thing, but now that I'm about to leave, I realize how much I loved living with all these people. I will remember our many movie nights at home, brunches, tennis games with Rafa and Sofia, nights out at Ferry with "Juan" and Ajith, long discussions with Eli, and the bowling night with everyone. I will never thank you, Marija, enough for everything you did during this thesis. I could not have dreamed of having a better supervisor. Your enthusiasm fueled my envy to continue and get more results even in the most difficult times. This same motivation pairs with curiosity. I cannot remember the number of hours we talked about the results' meaning and how I could validate the theory. Our meetings always started with the same ritual: I would arrive in the room, start talking about my thoughts, and you would tell me, "should we get a coffee first?". This small sentence reveals your high capacity for empathy and carefulness towards people. I was always amused when we walked in the corridors, and literally, everyone would come and talk with you. In a word, I would say that you are "une personne solaire" as french people say. We say this about people with positive energy who can communicate it to others. But I'm sure Maiko will know it better as these nine months together proved he was fluent in French.

"Comment ça va mon ami ?". This is the sentence I heard the most during my thesis. I have to say that I needed it when we had a casting session at 9 am. Thank you very much, Maiko,, for your help during my thesis. Your many tips helped me put my knowledge into perspective to make the right choices. I truly enjoyed working with you.

I also want to thank Oguzhan for the inspiration he gave me to work on this topic. His course, Concrete Forensic, became one of my favorite courses during my master's degree. Thank you for your advice, especially at the beginning of my thesis when I had the most difficulty structuring it. I want to thank Marcel for his great patience and wise advice. His advice particularly helped me when organizing my defense and writing my thesis.

I would like to thank Arjan, who helped me greatly using the ESEM-EDS. I know that this tool means a lot to you, and I want to thank you for trusting me. Thank you for allowing me to use ESEM-EDS on my own.

Lastly, I would like to thank my family, especially my mother and sisters, for always supporting me in my projects. You are my sunshine. I can't wait to spend more time with you.

Abstract

This master's thesis provides knowledge on non-destructive testing of cement and supplementary cementitious materials composition in concrete with a handheld X-ray Fluorescence analyser.

Today, concrete production is responsible for 8% of the world's CO_2 emissions. Recycling concrete material can directly contribute to the reduction of CO_2 emissions. This process is costly and time-consuming. A possible solution would be to use a handheld X-Ray fluorescence spectrometer on-site to determine the concrete chemical composition.

No existing research indicates if concrete identification with a handheld X-Ray Fluorescence analyser is possible. This thesis intends to prove that this technique can differentiate concrete with various chemical composition. Fourteen

concrete cubes of fourteen different chemical compositions were analysed to fulfil this objective. The fourteen compositions reflect the concrete design used in the Netherlands. Experimental programs conducted on the concrete revealed the impact of different factors on the results obtained from the handheld-XRF. These factors include measurement time, moisture, surface carbonation, and matrix effect. Each factor impacts various oxides in different proportions, leading to distinct patterns. After investigating their impacts, a protocol was written to test all the mixes. Finally, the reproducibility of the protocol was assessed, and the mixes were tested using the protocol.

The primary outcome of this thesis is proof that twelve of the fourteen mixes were differentiated based on their alumina content. This oxide proved to be less impacted by moisture and surface carbonation than the other oxides. The influence of the different factors on measurements was identified and quantified. These studies also revealed that twenty measurements were sufficient to identify the mixes. The protocol improved the control of the factors but also appeared limited by the concrete matrix.

A possible approach to circumvent this problem would be considering oxides content as thresholds rather than numbers. Determining these thresholds requires testing many samples. Another further study is the possibility of reducing the impact of moisture and surface carbonation on-site.

Contents

1	Int	roduction	1
	1.1	Research background	1
		1.1.1 Production of concrete	1
		1.1.2 Construction and Demolition Waste	2
	1.2	Research aim and objectives	3
	1.3	Research methodology	4
	1.4	Thesis outline	5
2	Lite	rature review on the composition of concrete in the Netherlands	
	and	the tools used to test its chemical composition	7
	2.1	Chemical composition of concrete	8
		2.1.1 Aggregates	8
		2.1.2 Cementitious Materials	3
	2.2	Techniques to test concrete chemical composition 1	7
		2.2.1 Destructive techniques	7
		2.2.2 Non-destructive techniques	:3
3	Exp	perimental program 2	6
	3.1	Raw Materials	26
		3.1.1 Aggregate	26
		3.1.2 Cementitious materials	29
	3.2	Mix design	0
	3.3	Methods	2
		3.3.1 Bruker S1 Titan 800 hXRF	2
		3.3.2 ESEM-EDS	52
		3.3.3 X-Ray Fluorescence	3
	3.4	Calibration	6
	3.5	Setup to compare results between hXRF and ESEM-EDS measure-	
		ments	6
		3.5.1 3D printed moulds	6
		3.5.2 Cutting the samples for EDS measurements	0
	3.6	Tests to determine the influential factors on hXRF measurements . 4	1
		3.6.1 Impact of the sample edges	1
		3.6.2 Measurement time	2

		3.6.3 Acquisition pattern
		3.6.4 Moisture impact and number of points
		3.6.5 Surface carbonation
		3.6.6 Presence of aggregates at the surface
	3.7	Code
		3.7.1 Code to randomize the choice of values
		3.7.2 Code to read and modify Excel sheets
4	Kes	Eactors impacting the measurements 50
	4.1	4.1.1 Impact of the sample edges 50
		4.1.1 Impact of the sample cuges
		4.1.2 Medsurement time
		4.1.5 Acquisition pattern
		4.1.4 Moisture impact and number of points
		4.1.6 Presence of aggregates at the surface 64
	4 2	Guideline and reproducibility 68
	1.4	4.2.1 Guideline 68
		4.2.2 Reproducibility 71
	43	Impact of the grading of the aggregates 74
	4.4	Overview of the chemical composition for concrete blended mix-
		tures
5	Dise	cussion 77
6	Con	clusion and Recommendation 82
	6.1	Conclusion
	6.2	Recommendation
A		87
	A.1	Formula
	A.2	Definition
B	Tab	les 88
С	Cur	ve plots and graphics 91
	C.1	
	C.2	Impact of the sample edges
	C.3	Impact of the sample edges (bell curves)
		Measurement time of 10, 20, 30 seconds
	U.5	KSD for measurement time of 10, 20, 30 seconds
		Measurement time of 20, 60 seconds
		Acquisition pattern for ovide
		Moisture impact
	U.9	

List of Tables

2.1	Cement chemists' notation	8
2.2	Maximum size for the aggregates in different editions of the Gewapen	d
	Betonvoorschriften (G.B.V)	9
2.3	Chemical composition of the river gravel coming from the Rhine	
	and Meuse area	10
2.4	Chemical composition of siliceous crushed rocks from the Nether-	
	lands	10
2.5	Chemical composition of Dutch river sand	11
2.6	Chemical composition of Dutch fine RCA	13
2.7	Chemical composition of CEM I 42.5 Portland cement	14
2.8	Chemical composition of low-calcium fly ashes in the Netherlands	15
2.9	Chemical composition of ground granulated blast furnace slag in	
	the Netherlands	16
3 1	Table of the sieving of different aggregate mixes based on the norm	
0.1	NEN-EN 12620	28
3.2	Table containing the total use of concrete in 1990, 2010, and 2017	20
0.2	in the Netherlands	29
3.3	Table of the chemical composition of the different powders tested	
	with a desktop-XRF	30
3.4	Table comparing the main properties between the hXRF and the	
	ESEM-EDS techniques	33
4.1	Table of the data quality criteria in terms of precision	54
4.2	Table of the relative standard deviation for the different oxides as	
	a function of the time for 60 points	55
4.3	Table of the percentage error for the different oxides as a function	
	of the time for 60 points.	57
4.4	lable of the percentage error between the regular value and the	50
4 5	Table of the notice between Cool on d SiO. for the membras of	59
4.5	Table of the ratio between CaO and StO_2 for the regular pattern	59
4.6	Evolution of the weight of the concrete cube in the climate cham-	60
	ber at 60° and 0° relative number 10°	60

4.7	Table containing the average over 20 points of the P/A ratio and	
	the area covered by paste and aggregates	66
4.8	Ratio between Al_2O_3 , SO_3 , K_2O , TiO_2	73
5.1	Percentage error of the different oxides for ordinary Portland cement	79
B. 1	Cement chemists' notation	88
B.2	Mineralogical information given by techniques on concrete	88
B.3	Table of the sieving of aggregates with the norm NEN-EN 12620 in	
	percent	89
B.4	Density of the compounds contained in concrete	89
B.5	Composition of the 16 mixes	89
B.6	Repartition of each element present at the surface in percent	90

List of Figures

1.1	Demand for cement in the period between 1970 and 2050	2
1.2	Appearance of a natural and a recycled aggregate in concrete	3
1.3	Thesis outline	6
2.1	Recycled concrete aggregates production in the Netherlands in 2015	12
2.2	Graph representing the polarized light microscope	18
2.3	Graph representing the inductively coupled plasma	19
2.4	Graph representing the energy dispersive X-ray fluorescence spec-	
	trometer	20
2.5	Graph representing the secondary electron microscope-energy dis-	
	persive X-ray spectroscopy	21
2.6	Graph representing the laser induced breakdown spectroscopy	22
2.7	Graph representing the handheld X-ray fluorescence spectrometer	24
3.1	Quartering of 4/32 mm aggregates	27
3.2	Gradation curves of the different aggregates batches (0/8, 0/16, 0/32)	29
3.3	Bruker S1 Titan X-ray analyser	32
3.4	Emission of characteristic X-rays	34
3.5	Photon scattering	34
3.6	Enhancement effect between two different elements	35
3.7	Mould for drawing the 9 squares on the concrete surface	37
3.8	Point acquisition on the concrete surface	37
3.9	Plastic mould used to draw the contour of the area for ESEM-EDS	
	and observation of the area under ESEM-EDS	38
3.10	Modelisation and picture of the plastic mould piece created to fit	~ ~
	the hXRF during measurements	39
3.11	Number associated to the hXRF and ESEM-EDS results	40
3.12	Saws used for preparing ESEM-EDS samples	41
3.13	Climate chamber Nuve 1K120	41
3.14	Design of the regular patterns	43
3.15	Graphic representing the absorption of X-rays by Water	44
5.10 2.17	Inne name for the surface carbonation of samples	40
3.1 <i>1</i> 2.10	Code to greate the wester r containing random values	40
J.10	Code to create the vector r containing random values	4Ö

3.19	Code to read and modify the tables in the Excel sheets	48
4.1	Evolution of the <i>CaO</i> content across the length of the concrete surface	51
4.2	Bell curve of the measurements done through the length of the cube	52
4.3	Diagram of the weight percentage as a function of the number of	54
4.4	Curve of the evolution of the relative standard deviation for SiO_2	54
	and <i>CaO</i>	56
4.5	Bell curves of the weight percentage obtained with a random and	
16	regular pattern for CaO and SiO_2	58
4.0	SiO_2, Al_2O_3	61
4.7	Impact of the moisture on the weight percentage of Fe_2O_3 , CaO_3 ,	
	SiO_2, Al_2O_3 with the standard error area around the measurements	<u> </u>
48	done in wet condition I_{max} Impact of the carbonation on the weight percentage for SiO_2 and	62
1.0	CaO	63
4.9	Comparison of the mapping and picture for points 1, 2, and 3	65
4.10	Impact of matrix heterogeneity on measurements	66
4.11	based concrete	68
4.12	Guideline for the measurements done with the ESEM-EDS	70
4.13	Test of the reproducibility with two cubes of CEM I-based concrete	
<u> </u>	for CaO and SiO_2	71
1.11	ing 10% GGBFS and 10%FA for CaO and Al_2O_3	72
4.15	Impact of the grading of the aggregates on the SiO_2 content	74
4.16	Weight percentage of Fe_2O_3 and Al_2O_3 for all the mixes designed	
		75
5.1	Mapping of the magnesium at the surface	78
C.1	Sieve analysis grading curve for different fractions	91
C.2	Pictures of the different types of sealing done for concrete samples	92
C.3	Cutting pattern for the three concrete cube surfaces	92
C. 4	smaller sample	93
C.5	Drawing of the points and square delimitation on the concrete sur-	
	face	93
C.6	Picture of the six moulds created to position the hXRF	94
U./	From the automatic frequency of the concrete From the length of the concrete	94
0.0	surface	96

C.9 Bell curves of the oxides content through the length of the concrete	
surface	98
C.10 Evolution of the oxides content versus the number of points for 10,	
20, 30 seconds	100
C.11 Evolution of the RSD for the oxides versus the number of points	
for 10, 20, 30 seconds	102
C.12 Evolution of the oxides content versus the number of points for 30,	
60 seconds	104
C.13 Evolution of the RSD for the oxides versus the number of points	
for 30, 60 seconds	106
C.14 Bell curves of <i>CaO</i> oxide for random and reguar patterns	107
C.14 Bell curves of SiO_2 oxide for random and reguar patterns	108
C.14 Bell curves of Al_2O_3 oxide for random and reguar patterns \ldots	109
C.14 Bell curves of Fe_2O_3 oxide for random and reguar patterns \ldots	110
C.14 Bell curves of MgO oxide for random and reguar patterns	111
C.14 Bell curves of SO_3 oxide for random and reguar patterns	112
C.14 Bell curves of P_2O_5 oxide for random and reguar patterns	113
C.14 Bell curves of T_1O_2 oxide for random and regular patterns	114
C.14 Bell curves of K_2O oxide for random and reguar patterns	115
C.14 Bell curves of MnO oxide for random and reguar patterns	116
C.15 Curves of the impact of moisture on the different oxides	118
C.16 Curve of concrete tested in dry and wet condition with the stan-	
dard error area plotted on the curve representing the wet condi-	100
	120
C.17 Curves of the impact of surface carbonation on the different oxides	122
C.18 Reason to hip the cube on the left	123
C.19 Guideline of the experiments led with the nXRF and SEM-EDS	124
C.20 Test of the reproducibility with two cubes of CEM I-based concrete	120
ing 10% CCRES and 10% EA	100
Ing 10% GGBFS and 10%FA	120
C.22 Maight percentage for all the surfaces designed in this thesis	130
C.25 weight percentage for all the surfaces designed in this thesis	132
0.24 weight percentage for an the surfaces designed in this thesis	134

Abreviation

XRF	X-Ray Fluorescence			
hXRF	handheld X-Ray Fluorescence analyzer			
PLM	LM Polarized light microscopy			
EDX	Energy Dispersive X-ray			
ICP	Inductively Coupled Plasma			
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry			
ICP-MS	Inductively coupled Plasma Mass Spectroscopy			
SDD	Silicon-Drift Detector			
CCD	Charged-Coupled Device			
BSE	Backscattered Electrons			
RH	Relative Humidity			
CDW	Construction and Demolition Waste			
RCA	Recycled Concrete Aggregates			
fRCA	Fine Recycled Concrete Aggregates			
NA	Natural Aggregates			
G.B.V	Gewapend Betonvoorschriften			
TNO	Nederlandse Organisatie voor Toegepast Natuurwetenschap- pelijk Onderzoek			
СН	Calcium Hydroxide			
CSH	Calcium Silica Hydroxide			
LOI	Loss Of Ignition			

Units

kV	Kilovolt
ppm	Part Per million
ppt	part per trillion
mm	Millimeters
R	Röntgen
Gy	Gray
Sv	Sievert
$Gy \cdot h^{-1}$	Dose rate

For X-rays and gamma rays:

1R = 10mGy = 10mSv

Chapter 1

Introduction

1.1 Research background

The first part of this introduction describes the concrete production and the second part outlines sustainable production of concrete.

1.1.1 Production of concrete

Concrete is made of aggregates, cementitious materials, and water. Aggregates represent the main component in concrete by its volume. On average the ratio between paste and aggregates is around 1:4. The paste is the other main constituent of concrete. Paste is obtained after the reaction of water and cement. It acts as a binder between the aggregates. Cement is mainly made of limestone, chalk, shale, marl, and clay, while aggregates composition is mainly sand, gravel, or crushed rocks. All of these components are extracted from the environment.

Concrete is the second most used material by humans on earth after water. In 2021, over 10 billion tons of concrete were produced in the world [1] .The production of a ton of concrete releases the equivalent of approximately a ton of CO_2 in the atmosphere [2]. Thus, in 2021 the total production of concrete represented 8% of the total emission of CO_2 around the world [3]. Those numbers reflecting the pollution created by concrete do not even consider the environmental impact caused by the extraction of new raw materials. The construction sector consumes approximately half of the raw materials extracted in the world [2]. Extracting raw materials for concrete production leads to the destruction of fragile environments such as topsoil, subsoil, and river beds which profoundly impact the wildlife in and around the extraction area. The available amount of raw materials is decreasing as most of the countries value and protect nature to fight climate change. Demand for concrete will keep rising in the following decades, as it can be seen in the figure 1.1 depicting the time versus the demand for cement.



Figure 1.1: Demand for cement in the period between 1970 and 2050. Reproduced from [2].

Nevertheless, the available stock of natural materials is decreasing and alternatives need to be found for replacement of aggregates and cement in concrete. One of the optimal solution to solve both issues would be to up-cycle Construction and Demolition Waste (CDW).

1.1.2 Construction and Demolition Waste

Companies will have to find a way to replace the use of raw materials to keep the price of concrete affordable if their stock depletes. In 2006, the price of recycled concrete aggregates(RCA) was already lower by 20% compared to the one for natural aggregates [4]. Furthermore, this price difference is potentially set to widen due to increasing taxation on raw materials. Elsewhere, production of concrete kept rising during the twentieth century, as it can be seen in the figure 1.1 and a recent report estimates that the average lifetime of concrete structures lies between 50 and 100 years [5]. Thus, the amount of CDW should keep increasing and by the same time the amount of RCA available should rise too.

All the reasons previously mentioned led governments and companies to vote agreement to develop a strategy towards the creation of a a circular economy for the concrete components. In 2018, fifty of the most prominent actors in the construction domain signed the Betonakkord to make the concrete industry more sustainable by 2030 in the Netherlands. This agreement stipulates that all the materials already used for concrete should be reused in a fully-circular economy by 2050 [6]. This statement implies that the recycling system should be optimal to avoid any sort of waste.

Presently, concrete in its wholeness cannot be fully recycled. The process used to create concrete is irreversible. During hydration of the cement new reaction product are formed by the rearrangement of oxides contained in the cement powder. Until now, no action can be done to reverse those hydration mechanisms to obtain cement from paste. However, most of the concrete is made of aggregates which can be recycled.

After demolition of a concrete structure, concrete is further crushed to separate aggregates and remove the paste. This process is not optimal and some of the paste stays on the surface of the aggregates, as shown in the figure 1.2. The chemical composition of the paste differs due to the type, the amount of cementitious materials used and the exposure condition of the original concrete. This paste might have an impact on new concrete and in some cases it leads to early damage. Therefore, it is important to characterize concrete before demolition of the structure.



Figure 1.2: Appearance of a natural and a recycled aggregate in concrete. Reproduced from [7].

CDW plants, in general, need at least 170 tons of waste per hour to be costeffective [8]. This later point generates some difficulties for CDW plants to select and sort the quality of concrete streams. Presently, it is cheaper for them to mix all the batches of CDW and down-cycle the aggregates rather than sorting the uncontaminated aggregates and recycling them separately as high-quality RCA. A way to reclaim a maximum amount of reusable materials would be to evaluate the quality of the concrete before the decommissioning of a building or a structure.

1.2 Research aim and objectives

The main objective of this thesis is to demonstrate how a handheld X-ray fluorescence analyzer can be used to differentiate concrete mixes based on the composition of their chemical components. The research is driven by the following objectives :

- Determine and quantify the impact of the different factors influencing the results obtained with an handheld X-ray Fluorescence analyzer (hXRF).
- Propose a guideline to lower the impact of the factors on the measurements acquired with an hXRF.
- Differentiate the type of concrete based on their chemical composition.

1.3 Research methodology

First, a literature review was done to identify the most used material in concrete in the Netherlands. The research suggested using different sizes of river gravel, as well as three types of cementitious materials: CEM I 42.5N, fly ashes (FA) and ground granulated blast furnace slag (GGBFS) in different proportions.

The choice of concrete mixes was motivated by the quantity of concrete produced for each mix in the Netherlands. The choice of the mixes was also driven by the idea of having a wide classification of concrete mixes.

This resulted in the design of fourteen mixes with the content of slag ranging from 10 to 90% and fly ash from 10 to 40% in addition to CEM I. Two extra mixes were designed to study the impact of the aggregates gradation on the hXRF measurements.

The difficulty to create a classification with the hXRF resulted from the absence of knowledge on the use of the hXRF on concrete. To prevent this, it was decided to use a well-known destructive technique known as Energy Dispersive Spectrometry (EDS). The choice was determined by the ability to control the environment during the test, the opportunity to observe the area before analysis, and the ability to test large samples.

The comparison of two techniques used on a heterogeneous material such as concrete requires assuring that the area analyzed under both types of equipment would be identical. The solution to this problem was to create 3D-printed shapes that would maintain the hXRF at predefined positions.

The factors impacting the results were first analyzed to establish a reliable identification of a concrete mix using an hXRF. These results motivated the creation of a protocol to improve the reproducibility of the tests. The various mixes were tested according to this protocol. Finally, mixes with different gradations were tested.

The identification of the factors affecting the results arose from two different sources. First, some of the previous studies pointed out the impact of some external factors to the sample: measurement time, moisture and representativity of the results. Additionally, internal factors within concrete were predicted and revealed after the preliminary measurements on CM I-based concrete, including the presence of aggregates, geometry of the cubes, and surface carbonation.

Each factor was studied independently. Moisture, measurement time, leaching and surface carbonation, presence of aggregates on the surface, and design of the cube were examined prior to the determination of the representativity of the results. The moisture impact was studied by wetting and drying the same cube. Then, measurement time influence was measured at the same spot of the cube by varying the beam time. Surface carbonation impact was detected at the beginning when the cubes were left in contact with air and humidity for a long time. The repercution of the presence of aggregates on the results was confirmed by analyzing the surface under the microscope as well as analyzing the surface with EDS. Finally, the influence of the geometry was studied by applying hXRF at the edge of the cube. From all those experiments, the number of points was determined to provide representative results.

A guideline was written after identifying all the impacting factors as well as comparing the results with the chosen destructive technique. Two cubes cured in identical ways were then tested using the guideline to study the reproducibility of the results. Finally, this guideline was applied to all the different mixes.

1.4 Thesis outline

The thesis outline is depicted in figure 1.3. **Chapter 1** presents the background for this research. **Chapter 2** revises the literature on the composition of concrete in the Netherlands and the equipment used for the analysis of concrete. **Chapter 3** presents the methods used to answer the aim of this thesis and the objectives. It contains five different sections. Those sections are the choice of the materials, mix design, methods, set-up to compare ESEM-EDS to hXRF results and the code created to perform data analysis. The results are presented in **Chapter 4**. A procedure was written to reduce the impact of those factors, and, then applied to the measurements on the different concrete mixes. These steps were also described in **Chapter 4**. **Chapter 5** discusses the reason of the impossibility to detect magnesium, gives a definition of the lightweight elements in concrete, presents the oxides to compare in order to differentiate the mixes, and defines the optimal number of points to obtain reproducible results. Finally, **Chapter 6** draws conclusions on the experiments and the recommendations for the upcoming research on this topic.





Chapter 2

Literature review on the composition of concrete in the Netherlands and the tools used to test its chemical composition

2.1 Chemical composition of concrete

This chapter provides an overview of the different types of cementitious materials and aggregates used to make concrete. Aggregates can be differentiated regarding their chemical composition and their size. The distinction based on their chemical composition will not be presented here since siliceous aggregates have always been used in a larger proportion than calcareous aggregates in the Netherlands. The most accessible aggregates in the Netherlands are river gravel from the Rhine and Meuse Delta as well as siliceous crushed rocks from Germany and Belgium.

Cementitious materials are presented in the second section of this chapter. The cementitious materials presented in this section are Portland cement, fly ashes and ground granulated blast furnace slag. Fly ashes and ground granulated blast furnace slag are by-products of the industry. They are used as supplementary materials to replace cement. Their use in concrete will change concrete properties and lower concrete footprint.

In the literature review, we will use the "cement chemists' notation" simple letters to replace oxides formulae to simplify equations. The table **B.1** links letters to the corresponding oxide.

Table 2.1: Cement chemists' notation

Oxide	Ca0	SiO ₂	Al_2O_3	Fe_2O_3	H_2O	Na_2O	<i>K</i> ₂ 0	SO_3	MgO	CO_2
Symbol	С	S	А	F	Н	N	K	\overline{S}	М	\overline{C}

2.1.1 Aggregates

The European norm NEN-EN 12620:2002+A1:2008 [9] defines aggregates as "granular material used in construction." Aggregates may be natural, manufactured, or recycled. Aggregates are one of the main constituents of concrete besides water and cement. Their use improves the workability and strength of concrete. The Dutch industry requires around 159 million tonnes (Mt) of aggregates yearly, mainly for the construction industry [10]. This amount includes 90 Mt of sand, 4.9 Mt of gravel, 3.9 Mt of clay, and 1.6 Mt of carbonate rocks. The Netherlands produces around 101 Mt of aggregates per year [10]. The rest of the aggregates are imported.

Among the aggregates, 75% of them are used in concrete, 15% in masonry mortars, and the rest is used for a wide range of purposes such as the production of asphalt and bricks [10]. Each of these applications requires specific grain-size distribution of the aggregates. Grain size distribution is of a primary importance in concrete mixes.

The size of aggregates contained in concrete ranges from the order of 32 mm down to particles less than one-tenth of a millimeter in cross-section [11]. Their size divides them into three subsections: coarse aggregate, fine aggregate, and fillers. Coarse aggregates are defined under the norm NEN-EN 12620:2002+A1:2008 as aggregates with a size larger than 4 mm in terms of upper sieve size. The same norm defines fine aggregates as aggregates with an upper sieve size smaller or equal to 4 mm. In addition to these two types of aggregates, concrete companies use fillers for their low cost and physical properties. Fillers are aggregates with a size below 63 μm [11].

Coarse Aggregates

The maximum size of aggregates contained in concrete evolved for different reasons, including workability and strength. During the past century, the maximum size of the aggregates in the Netherlands alternated between 38 and 60 mm (table 2.2). More recently, the size of the aggregates is limited to 16 mm except in some particular case where it extends to 32 mm.

Table 2.2: Maximum size for the aggregates in different editions of the Gewapend Betonvoorschriften (G.B.V) [11].

	Maximum size (mm)
G.B.V 1918	60
G.B.V 1930	<38
G.B.V 1940	<46
G.B.V 1950	<46
G.B.V 1962	<46

The Netherlands uses two main groups of coarse aggregates to create their mixes: gravel and crushed rock. The environment and process of extraction define the shape and composition of these two groups of aggregates. The production of crushed aggregates is done by extracting stone blocks and crushing them. This operation gives them a rough surface. Gravels lie at the bottom of rivers and are dredged by boat. Their environment gives them a round and smooth surface.

Gravel

Gravel represents the main source of aggregates used in the Netherlands since 1918. Gravel are available in large quantities and cheap compared to crushed rocks produced in Germany and Belgium [11]. The chemical composition of aggregates varies significantly with their provenance. Three types of gravel were exploited in the Netherlands: river gravel, pit gravel, and sea gravel. All of these aggregates are mainly composed of siliceous aggregates, and in the case of sea aggregates of chert [11]. The use of sea gravel was limited due to the high content of sulfate and chloride coming from seawater. Eastern Netherlands mainly used pit gravel due to its local availability. The rest of the Netherlands also used this type of aggregates in the early twentieth century. However, pit gravels were rapidly replaced by river gravel as transport made it cheaper than pit gravel in those regions. Finally, river gravel was the primary type of gravel used for construction.

Rhine and Meuse Delta areas were and stayed the major extraction region for gravel. The composition of river gravel from these areas has been determined and can be found in table 2.3.

Table 2.3: Chemical composition of the river gravel coming from the Rhine and Meuse areas [12].

Constituent Materials	Oxide (%)	
CaO	0.7	
SiO ₂	96.2	
Al_2O_3	1.1	
Cl	1.6	
K ₂ O	0.4	

Crushed rocks

During the twenthieth century, crushed rocks were preferred to gravel for two main reasons. Crushed rocks have a stronger bond with cement paste due to their rough surface [11]. A higher surface area implies a stronger bond and conversely, a smooth surface weakens the interfacial transition zone (ITZ) in concrete. Furthermore, the freshly broken surface of the aggregates was less subjected to contamination. The main parent rocks used were basalt, granite, and porphyry.

In the Netherlands, siliceous crushed rocks were mainly used due to their availability as well as due to governmental recommendation.

Table 2.4: Chemical composition of siliceous crushed rocks from the Netherlands [11].

Constituent Materials	Oxide(%)	
SiO_2	92.3	
Fe_2O_3	2.4	
Al_2O_3	2.2	
Cl	2.7	
K ₂ O	0.4	

Fine Aggregates

The most commonly used fine aggregate in the Netherlands has been natural sand [11]. The origin of the sand varies from river, dunes, or fields and peat. However, in the early '20s mainly river sand was used. It came from the river beds of the Rhine and Meuse but also sometimes from the river Waal and Lek. After 1930, the provenance of fine aggregates was not anymore restrained to river sand and companies started using cheaper sand coming from different areas closer to the concrete plants [11]. The chemical composition of typical Dutch river sand can be found in the table 2.5.

Constituent Materials	Oxide (%)	
SiO ₂	94.9	
Al_2O_3	2.2	
K ₂ O	0.4	
Fe_2O_3	2.5	

Table 2.5: Chemical composition of Dutch river sand [12].

Recycled concrete aggregates

Recycled concrete aggregates (RCA) are seen under the norm NEN-EN 12620:2002+A1:2008 [9] as "aggregates resulting from the processing of inorganic material previously used in construction". This means that RCA are extracted from parent concrete to be repurposed. To do so, parent concrete is crushed and aggregates surrounded with paste are collected. The whole process of sorting and recycling CDW can be seen in the figure 2.1.

The Netherlands produces around 25 Mt of construction and demolition waste (CDW) each year [14]. The 95% of it is collected to be sorted out (roughly 24 Mt), the rest being judged as hazardous materials. Then, CDW is separated into different batches according to their origin (mineral waste, wood, plastic and metals). From this selection, 64% occurred to be mineral waste in 2015. Mineral wastes are recycled in diverse domains as new concrete, substitute material for natural sand in cementitious rendering and masonry mortars, road construction, filling material for geosynthetic reinforced structure and soil stabilization [15]. Seven million tons of coarse RCA and five million tons of fine RCA are produced every year [15]. Their recycling rate approaches 100% and represents around 20% of the aggregates used in the Netherlands [16]. However, as shown on the graph, only 5.3% of the RCA are re-used to create new concrete; the rest is down-cycled. 18.6% goes to site elevation for road and building, and 76% to road foundation [17].



Figure 2.1: Recycled concrete aggregates production in the Netherlands in 2015. Adapted from [13].

The properties of natural aggregates do not vary with time. Nevertheless, the chemical and mineralogical composition of paste depends on the parent mixing, recycling technique, and storage of the recycled concrete aggregates. Only coarse RCA are up-cycled, the rest of the RCA have unpredictable properties. The Netherlands does not sort out the concrete rubbles, and their chemical composition (mainly fine fraction) stays unknown. Fine RCA contains more cement paste than the coarse aggregate. So, their chemical composition varies considerably regarding their provenance as can be seen in the table 2.6. This table gives the chemical composition of three different batches (A,B,C) of Dutch RCA. Thus, European norms forbid their use in new concrete to avoid any early decay of the construction [9].

Constituent material	A (%)	B (%)	C (%)
SiO ₂	62.8	68.2	75.8
Al_2O_3	5.8	4.4	4.3
Fe_2O_3	3.3	2.0	1.7
CaO	22.5	20.4	14.4
MgO	1.5	1.6	0.9
Na ₂ O	0.6	0.5	0.4
K ₂ O	1.5	1.2	1.1
TiO ₂	0.5	0.3	0.3
SO ₃	1.16	0.91	0.89
Cl	0.03	0.07	0.04

Table 2.6: Chemical composition of Dutch fine RCA [18].

In general, coarse RCA consist of 65-70% of aggregates and 30-35% of old cement paste by volume [19]. This layer of cement paste on RCA will affect the quality of the fresh concrete for different reasons :

- by entailing a greater porosity than natural aggregates which leads to higher absorption of water [20],
- elements such as sulfates and chloride (if present in cement paste on RCA) can contaminate the new concrete [20],
- presence of microcracks inside cement paste and RCA [21],
- increase of the transition zone (ITZ) between old cement paste and natural aggregates, [19].
- lower friction resistance [19].

This lack of confidence in the quality of RCA and their highly heterogeneous chemical and mechanical properties create concern about their use. Thus, construction companies reuse only a small proportion of these RCA.

2.1.2 Cementitious Materials

Cementitious materials constitute one of the main components inside the concrete. They can be divided into two category: hydraulic cement and Supplementary Cementitious Materials (SCMs). Hydraulic cement reacts with water in a non-reversible process to form a strong paste that binds aggregates. SCMs contribute to develop properties of the concrete. They are added to the hydraulic cement to improve the workability of fresh concrete and to reduce the heat produced during the hydration process.
Portland cement

Portland cement is composed of four main compounds: tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetra-calcium aluminoferrite (C_4AF). C_3S is the major compound, it represents 55% to 65% of the cement by volume. C_2S covers 15% to 25% of the total volume, and C_3A occupies 8% to 14% of it. Finally, C_4AF stands for 8% to 12% of the volume [22]. Portland cement also contains a small amount of free lime and magnesia along with alkalies. Free lime corresponds to a certain amount of lime that did not burn during the process of calcination and will not react with water during hydration. Portland cement composition changes from one to another plant due to the composition of the raw materials source and the production process. An average chemical composition of Portland cement is shown in the table 2.7.

Constituent Materials (%)	CEM I 42.5N
CaO	62.6
SiO ₂	19.6
Al_2O_3	4.8
Fe ₂ O ₃	3.0
MgO	1.8
K ₂ O	0.6
Na ₂ O	0.4
S	1.4
TiO ₂	0.3
P_2O_5	0.3
LOI ¹	2.8

Table 2.7: Chemical composition of CEM I 42.5 Portland cement [23].

Supplementary cementitious materials

SCMs contribute to the properties of hardened concrete by the pozzolanic and hydraulic reactions. They are often added to concrete to increase concrete durability to improve its workability and decrease its shrinkage. These materials also improve the environmental impact of concrete by reuse of by-products from industry. The two most used SCMs, ground granulated blast furnace slag and fly ashes, are respectively by-product of the iron industry and coal combustion by-product in power plants.

Fly ashes

Loss of ignition (LOI): mass loss caused by the heating of raw materials in cement production

Fly ash results from the stack gases produced by burning pulverized coal in thermal power plants [24]. In 2000, 600 Mt of fly ash were produced worldwide. Instead of land-filling this waste which would cause massive pollution of the environment, European countries like the Netherlands decided to partly reuse fly-ash in the production of concrete. This tendency has been increased with the will to reduce the CO_2 footprint of concrete. Around 30% of the fly ashes produced in Europe are reused in concrete [25]. The technical requirements for the use of fly ashes are referenced in the European Standard NEN-EN 450.

The composition of fly ashes (FA) varies greatly regarding the provenance due to the type of coal burned in the power plant. It is a fine powder composed mainly of quartz, mullite, magnetite, hematite, agglomerates, and unburned particles of coal. Anthracite and bituminous coal generally produce coal with a high concentration of silica (SiO_2), aluminum oxide (Al_2O_3), and a low content of calcium oxide (CaO). Reversely, lignite and sub-bituminous coal tend to produce fly ash rich in calcium oxide (CaO) content but a low amount of aluminum oxide (Al_2O_3) and silicon dioxide (SiO_2) [24]. They are mostly composed of the three previous oxide and contain in lower amount: magnesium oxide (MgO), sodium oxide (Na_2O), titanium dioxide (TiO_2), sulfur trioxide (SO_3) and potassium dioxide (K_2O). They also contain residual unburned coal. Fly ash is sorted into two different types depending on its content in calcium oxide. The siliceous fly ash, called low-calcium fly ash contains less than 10% of CaO. The other type contains more than 10% of calcium and it is called high-calcium fly ash [24].

Constituent materials (%)	fly ashes
SiO ₂	5.8
Al ₂ O ₃	23.8
Fe ₂ O ₃	7.2
CaO	4.8
MgO	1.5
Na ₂ O	0.8
K ₂ O	1.6
S	0.3
TiO ₂	1.2
P_2O_5	0.5
LOI	1.2

Table 2.8: Chemical composition of low-calcium fly ashes in the Netherlands [23].

Ground granulated blast furnace slag

Ground granulated blast furnace slag (GGBFS) is the by-product obtained during the production of molten iron [24]. Around 200 to 400 kilograms of liquid slag are produced for every ton of hot metal cast [24]. Liquid slag is then transformed into spherical pellets.

The composition of GGBFS depends on the process and the chemical composition of the molten slag iron. It contains mainly silica (SiO_2), aluminium oxide (Al_2O_3), calcium oxide (CaO), and magnesium oxide (MgO). Those oxides together represent 95% of the GGBFS composition. The table 2.9 depicts the chemical composition of Dutch GGBFS:

Table 2.9: Chemical composition of ground granulated blast furnace slag in th	e
Netherlands [23].	

Constituent materials (%)	GGBFS
SiO ₂	35.5
Al_2O_3	13.5
CaO	39.4
MgO	8.0
Na ₂ O	0.4
SO ₃	1.0
TiO ₂	1
Fe_2O_3	0.64
P_2O_5	0.009
K ₂ O	0.53
LOI	- 1.3

2.2 Techniques to test concrete chemical composition

This chapter aims to provide an overview of the various techniques used to analyse the composition of concrete. A detailed explanation will be provided on the destructive techniques, outlining the principles involved in detecting the composition of concrete. Subsequently, non-destructive techniques will be mentioned and elaborated upon in further detail, including their working principles. This comprehensive discussion aims to provide insight into the methods utilized for concrete composition analysis.

2.2.1 Destructive techniques

By definition, a destructive technique requires an extraction and destruction of the sample for the elemental analysis. This destruction might be done by cutting the sample, transform the sample into powder, or by digestion 1 .

Polarized Light Microscope

Polarized Light Microscope (PLM) is a contrast enhancing optical microscopy technique that modifies the appearance of the specimen by exploiting the optical properties specific to anisotropy. This technique provides surface qualitative and quantitative results. It reveals information on the chemical composition and morphology of the constituents in the sample. All anisotropic materials can be characterized by the capacity to act as a beamsplitter and divide light rays into two rays orthogonal to the sample, as depicted on the figure 2.2. Both rays will have different directions and different velocities. By measuring the difference in speed between the two beams, the PLM can determine the birefringence indices. This birefringence index is correlated to the colour of the components under the polarised light. Qualitative analysis of chemical composition can then be done using the depth of the sample and the birefringence index. In the case of concrete, PLM is used to detect crystalline structures. Thin sections with thickness equal to 50 μm are analysed as they let the light go through.

¹digestion is the action to dissolve a solid sample in a solution before testing them with Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)



Figure 2.2: Graph representing the polarized light microscope. Adapted from [26]

The PLM is composed of: a camera, an eyepiece, the analyser, the objectives, the polarizer and the light source. The polarizer and analyser are positioned in the light path. Those two filters are made of tiny crystallites oriented in the same direction and embedded in a transparent polymeric film [26]. The polarizer filters the white light and diffuses it in a single direction. The polarizer is located below the sample while the analyser is placed above the sample. After passing through the anisotropic sample, the beam will be split into two beams out of phase. The analyser is used to increase the contrast by ensuring that the two beams have the same amplitude while recombining. Finally, the digital camera will recombine the two rays and adjust the colour to the birefringence indice.

Inductively Coupled Plasma

Inductively Coupled Plasma (ICP) is a qualitative as well as quantitative destructive hard ionization method. It implies the full atomization of the sample during the test. The equipment is composed of two parts: the ICP and the equipment analysing the results. The information analysed by the spectrometer will differ. The Optical Emission Spectrometry (OES) will analyse the wavelength of the excited atoms or ions, while the Mass Spectrometry (MS) will measure their mass. The detection limit of the ICP-MS is lower than for ICP-OES (ppt versus ppm).



Figure 2.3: Graph representing the inductively coupled plasma. Reproduced from [27].

Samples analysed with this technique need first to be transformed into liquid by dissolving them with water or acid. After transforming the sample into a liquid, a peristaltic pump sucks the liquid and drives it to the nebulizer as can be observed on figure 2.3. The nebuliser will boost the speed of the liquid and turn a part of the liquid into an aerosol [28]. The bigger particles will flow in the drain. After passing through the nebulizer, the spray is introduced in the center of the spray chamber where the liquid is introduced in the plasma. The plasma de-solvates the aerosol into a solid, vaporises the solid into a gas and then dissociates the individual molecules into atoms [29]. The most common gas for this application is argon but more recently new ICP model replace Argon with Nitrogen to lower the cost. Plasma is an ionized gas obtained at a high temperature between 5000 K and 9000 K [30]. At this high temperature, electrons gravitating around the nucleus get excited and de-energize by releasing a photon [31]. These photons will be detected by the mass spectrometer or optical emission spectrometer, later analysed to be attributed to the corresponding element.

Energy Dispersive X-Ray Fluorescence Spectrometer

Energy Dispersive X-Ray Fluorescence Spectrometer (Desktop-XRF) is an element qualitative as well as quantitative technique. It exploits the X-ray fluorescence principle 3.3.3 by bombarding the surface of the sample with primary X-rays. Photons contained in the X-ray will excite the atoms in the sample to produce secondary X-rays [32]. Each element will send back X-rays with a characteristic wavelength which will be associated to the corresponding element by the detector.



Figure 2.4: Graph representing the energy dispersive X-ray fluorescence spectrometer. Adapted from [33].

As illustrated in the figure 2.4, a desktop-XRF apparatus consists of a power supply, a light path subsystem, a control circuit and a computer. The light path subsystems is responsible for emitting, receiving and counting the photons [32]. It includes a X-ray tube, filter, collimator and a detector. High-voltage power is supplied to the X-ray tube to produce primary X-rays. The collimator and filter are used to reduce the beam size and ensure that only primary X-rays with a particular energy will be generated. X-rays will irradiate the sample and stimulate the elements to emit secondary X-rays. These X-rays will be analysed by a CCD camera which will send the information as pulse counter to the computer. The detector sorts out the received photons regarding their energy and deduce the intensity from the count of the number of photons with identical energy [32].

Energy Dispersive X-ray Spectroscopy

Secondary electron Microscope-Energy Dispersive X-Ray Spectroscopy (SEM-EDS) is a qualitative and quantitative X-ray technique. It is composed of two different devices: a Secondary Electron Microscope (SEM) which will produce high magnification pictures along with an Energy Dispersive Spectrometer (EDS) which will identify and quantify the elements present inside concrete. SEM-EDS uses the X-Ray fluorescence principle as in the case of the desktop-XRF. However, rather than shooting photons on the sample, it will shoot electrons. Thus, the EDS hardware differs from the one for the desktop-XRF.



Figure 2.5: Graph representing the secondary electron microscope-energy dispersive X-ray Spectroscopy. Reproduced from [34].

The scanning microscope and sample chamber contains an electron gun to generate an electron beam. Then, a system made of an anode, a gun alignment coil and aperture will define the orientation and the size of the beam. The beam will go through the scanning coil where it will be swept into a linear or raster pattern. The beam will arrive in the vacuum chamber where it will hit the sample and produce secondary electrons, backscattered electrons, and X-rays. The secondary and backscattered electrons will be used by SEM to create highly magnified images and X-rays will be used to determine the elements present in the sample. Similar interaction as the one depicted in the section 3.3.3 will be encountered between the electrons and elemental particles inside the sample.

However, this technique, in contrast to the hXRF and desktop-XRF, requires a coating layer on top of non-conductive samples. A part of the electrons shot by the SEM-EDS stays trapped in the sample, causing an accumulation of negative charges. The negatively charged surface will repel the primary electrons and distort the beam [35]. A coating layer of approximatively 10 nm is applied on the surface of the sample to correct this effect. Generally, materials used to cover the surface of the sample are carbon, gold or palladium. A too thick coating layer might interfere with the emission of BSE, while a too thin film might not protect the sample against charge-up effect.

A new version of the SEM called 'Environmental Scanning Electron Microscopes' (ESEM-EDS) uses the electrostatic properties of moist air to circumvent the previously mentioned issue. This technique can only be applied to hydrous and moist materials [36].

Laser Induced Breakdown Spectroscopy (LIBS)

The LIBS technology is a qualitative as well as quantitative technique used in diverse domains such as metallurgy [37], biomedical field [38] or environmental study [37, 39, 40]. This technique can be brought on field and used to test solid, liquids or gaseous samples in real time [41]. The LIBS utilizes the properties of the light to detect the chemical composition of the samples. It will shoot highly energetic pulse laser beam on the sample for few nanoseconds. The high temperature of the laser will melt the sample into a plasma. This plasma will contain free atoms and ions [42]. When the plasma cools down, the electrons of the atoms and the ions de-energize themselves by releasing photons of particular wavelength. The emitted light is collected by the optical fiber coupled with a spectrometer. This spectrometer records usually light spectra ranging from ultraviolet to infrared.



Figure 2.6: Graph representing the laser induced breakdown spectroscopy. Adapted from [43].

The LIBS is composed of a laser, used as an excitation source. This laser commonly occurs to be a Nd: YAG with various wavelengths of 1064, 532, 355 or 266 nm [42–44]. It is oriented with a mirror and focused on the sample surface through the use of a focal-distance lens. A focused-silica fused lens is used to focus the emission of the plasma in an optical fiber. Finally, the spectra is recorded with the use of a high speed fiber spectrometer as well as intensified with the use of a charge-coupled device (CCD).

Its high accuracy permits to detect all the elements in the periodic table above hydrogen with an accuracy from few ppm to hundred of ppm depending of the chemical element. The sample analysed with the LIBS do not require to be prepared prior to the test since the sample surface will be ablated by the laser.

2.2.2 Non-destructive techniques

Non-destructive techniques correspond to techniques analysing the numerous properties of a given material without damaging it. These techniques can be used on-site to analyse materials with limited to no sample preparation [45]. In addition, the non-destructive techniques are cost-effective and time-efficient, allowing to obtain multiple measurements in a short period of time. However, due to the limited sample preparation, results will be more impacted by environmental conditions compared to destructive techniques. That is why, they are used to provide real-time or near-time decision support in addition to laboratory studies.

handheld X-ray Fluorescence spectrometer (hXRF)

handheld-XRF is a qualitative and semi-quantitative technique using the fluorescence properties of materials to analyse their composition (see section 2.2.1). This technique can be applied to many domains such as medicine ([46]), geology ([47]), archeology ([48]), or soil pollution ([49], [50]). This technique detects elements ranging from Mg to U [45]. Then it assigns these elements to the equivalent oxides. It uses mathematical models based on stoichiometry and the concentration of the elements found in the sample.

Handheld-XRF is made of 3 main components: an X-ray source, an X-ray detector, and electronics for signal processing, calculation, and displaying results [51]. The X-ray tube contains five parts: a cathode, an anode, an envelope, a housing, and a window. These five parts will generate X-rays with particular energy along with controlling the generated heat and excess radiation produced by the anode. The detector is made of six different parts: a collimator assembly, an electron trap, a window, a sensor, a Field Effect transistor (FET) as well as a detector cooling [52]. The detector converts the energy of the X-rays coming from the sample into a voltage signal of proportional size. Afterwards, the electronics will associate the elements with the signals received.

Recent hXRF are smaller and lighter (weight approximately 1 kg with the battery) with a charge capacity of 16 hours, making it one of the most favored onsite non-destructive techniques. Acquisition time varies between 60 and 120 seconds depending on the sample properties [54].



Figure 2.7: Graph representing the handheld X-ray fluorescence spectrometer. Adapted from [53].

Measurements obtained on-site cannot be as precise, sensitive, and accurate as those obtained in the laboratory due to sample preparation and environment [45]. This is due to several factors causing systematic bias, in which hXRF results are lower than laboratory analyses on the same sample. Factors affecting the measurements are: air contained between the tip and the specimen, moisture content, granularity, porosity, and heterogeneity of the sample. Moisture content and air will interfere with the X-ray beam and absorb X-rays. The heterogeneity of the sample includes two types of heterogeneity: the matrix composition and the distribution of the constituents inside the sample. The latter resides in the fact that the volume analysed by the hXRF is limited [55]. The window size is less than 1 cm^2 , and X-rays penetrate the sample with a depth up to approximately 1 mm, depending on the properties of the sample (density, chemical composition, position of the elements). In addition, lighter elements will emit X-rays with lower energy. So, these photons have a better chance of being trapped in the sample. In addition, SDD detectors need to receive more photons coming from lightweight elements. For instance, it requires only two ppm for iron to be detected by the hXRF while it needs at least 993 ppm for magnesium to be detected [54]. Thus, more X-rays needs to be detected for lightweight elements. The fact that X-rays from lightweight elements are easily absorbed and require to be in a larger number, makes it difficult to detect these elements accurately.

Nevertheless, the heterogeneity of the sample can be corrected by predicting the structure of the sample. This is done by using a calibration model incorporated into the software of the hXRF. Calibration corresponds to the transformation of signals received in the detector. A correlation is established between the weight percentage of elements (in part per million) and the intensity of X-rays (in counts). Two calibration modes exist for the analysis of sedimentary samples: the mining mode and the soil mode. These two modes have different algorithms and will measure different elements. The soil mode provides broad and easy coverage of low concentrations. In contrast, the mining mode has a higher accuracy for elements present in high concentrations. The former is more used for analysis and detection, while the latter is used for quantification [45]. If both trace and significant level elements are desired, the sample composition can be measured using the two modes without moving the analyser between the two measurements. A hybrid mode exists and is called the Geochem mode. This mode offers a compromise between the sensitive soil mode and the quantitative mining mode [45].

Chapter 3

Experimental program

This thesis aims to identify different concrete compositions using an hXRF. Sixteen mixes were designed with various chemical compositions and aggregate particle size distributions. The material choice is explained in section 3.1. The mix design of concrete is given in section 3.2.

A deeper understanding of the working principle of the hXRF and a table with more details about the hXRF and the ESEM-EDS are provided in section 3.3. Section 3.4 explains the calibration of the Bruker S1 Titan 800. Finally, section 3.5 explains the setup for comparison between ESEM-EDS and hXRF measurements. This includes the design of various plastic moulds to control the position of the points as well as the labeling of the samples.

3.1 Raw Materials

The choice of cementitious materials and aggregates was based on the literature review. In parallel to casting, powders of the raw materials present in the mixes were tested with desktop-XRF to determine their chemical composition. The chemical composition of raw materials helped to understand and predict the results obtained during the research.

3.1.1 Aggregate

The choice of the type of aggregate was based on the type of aggregate used in the Netherlands during the last century. The price of aggregates depends mostly on their transport. Therefore, they are mostly produced locally. In the Netherlands, the Rhine and Meuse Delta provide most of the aggregates: gravel and river sand. Their provenance has not differed much since the early twentieth century. However, the limitations of the allowed size in concrete evolved as explained in the table 2.2. TNO estimated the lifetime of concrete structures in the Netherlands to be between 50 and 100 years [5]. Thus, the impact of the size of the aggregates will be studied in addition to the differentiation of paste. Three different mixes containing aggregates with a maximum diameter of 8mm, 16mm, and 32mm will be used in this study. The rest of the mixes will contain 16mm aggregates, as commonly used in the Netherlands.

The grade of aggregates plays an influential role in the workability of concrete. The distribution of aggregates will be inhomogeneous if the workability is too low or too high. Hence, the 0-4 mm, 4-8 mm, 4-16 mm, and 4-32 mm aggregates were sieved according to European standard NEN-EN 12620. The aggregates were first screened manually in a sieving tower with a sieving size varying from 8 mm to 63 mm. Then, aggregates with a diameter smaller than 8 mm were screened in an automatic sieving tower with sieves from 63 μm to 8 mm. 4 kilograms of dried aggregates was sieved in the manual tower and then sieved in the automated tower. Only 1 kilogram was sieved in the case of the 0-4 mm mix due to weight limitation with the automatic sieving tower. Automatic sieving was done for 1 minute. In the case of manual sieving, the sieve was fixed on a wood rolling platform and then shaken for two minutes. Then, the content of each sieve was weighed.

The laboratory did not have 4-32 mm size aggregates ready for use. Therefore, 70 kilograms of this mix were ordered from Dyckerhoff Basal. The 70 kilograms were piled up in a circular stack as seen in the picture 3.1a. Then, this pile was split into four equal piles with a shovel. Two piles were discarded, and the rest was mixed, as seen in the picture 3.1c.



(a) Original pile of aggregates.

(b) Cross separation with a shovel.

(c) Discard half of two piles

Figure 3.1: Quartering of 4/32 mm aggregates.

This process was repeated until the pile weighed approximately 4 kilograms. This procedure was done to maintain a homogeneous gradation of the mix. The sieving results can be found in table 3.1.

Sieve diameter (mm)	0-4 mm (g)	4-8 mm (g)	4-16 mm (g)	4-32 mm (g)
63	0	0	0	0
31.5	0	0	0	0
16	0	0	40.5	2887
8	0	346.9	2479	534
4	73.2	3753.3	1235.8	464.9
2	86.7	57.9	132.5	38.4
1	112.6	12.7	21.6	7
0.5	267.4	7.4	12.5	4.1
0.25	338.5	9.2	18.5	4.7
0.125	69.5	3	12.1	4.2
0.063	6.2	0	12.1	5.4
Total	954.1	4190.4	3964.6	3944.3

Table 3.1: Table of the sieving of different aggregate mixes based on the norm NEN-EN 12620.

The sand percentage was calculated based on the formula contained in the paper [56]. This method requires the percentage of aggregates retained below the 1 mm sieve. The table of sieving in percentage can be found in the appendix B.3.

Example calculation of the sand percentage for 0-32 mm aggregates:

$$P_{z} = \frac{x_{1mm}^{theo} - x_{1mm}^{exp}}{x_{1mm}^{0-4} - x_{1mm}^{exp}}$$
(3.1)

P_z : Percentage of sand

 x_{1mm}^{theo} : Theoretical maximum of sand with a diameter of 1 mm or below. It can be found in the appendix on the curve C.1.

 x_{1mm}^{exp} : Percentage of sand with a diameter below 1 mm in the 4-8 mm, 4-16 mm, as well as 4-32 mm batches.

 x_{1mm}^{0-4} : Percentage of sand with a diameter below 1 mm in the 0-4 mm batch

In the case of 0-32 mm aggregate mix, $x_{1mm}^{theo} = 28\%$, $x_{1mm}^{exp} = 0.32\%$ and $x_{1mm}^{0-4} = 71.34\%$. After calculation, the P_z of this fraction was equal to 0.39. Thus, creating 0-32 mm concrete mix requires using 39% sand and 61% coarse aggregates. In the case of the 4-8 mm aggregates, $P_z = 0.57$, and in the case of the 4-16 mm aggregates, $P_z = 0.45$. Finally, the gradation curve of each mix was obtained by multiplying the amount of coarse and fine aggregates by their respective factors $(P_z \text{ and } 1 - P_z)$ and summing them.

Example calculation of the sand percentage for 0-32mm aggregates:

$$m_{4mm} = 73.2 \cdot 0.39 + 464.9 \cdot 0.61 = 312.13g \tag{3.2}$$

The resulting gradation curves are represented in Figure 3.2:



Figure 3.2: Gradation curves of the different aggregates batches (0/8, 0/16, 0/32).

Gradation curves need to remain in the area I to ensure mix workability. As seen on the curves in the appendix C.1, the curves corresponding to the three different batches (0/8, 0/16, 0/32) are located in this area. Thus, the quality of the mixes is optimal.

3.1.2 Cementitious materials

A literature review guided the choice of cementitious materials. The most used mix nowadays is CEM III-based concrete followed by CEM I-based concrete, CEM II-based concrete, as seen in the table 3.2.

Table 3.2: Table containing the total use of concrete in 1990, 2010, and 2017 in the Netherlands. Adopted from [57].

Type of	Total use of concrete (%)			
cement	1990	2010	2017	
CEM I	36	34	36	
CEM II	7	2.6	7	
CEM III/A	0	10	15	
CEM III/B	57	52	40	
CEM V	0	1.7	2.2	

CEM I 42.5N cement was chosen for the mixes in this thesis. As the literature review explains, GGBFS and FA are the most common types of SCMs. The amount of SCMs varies for each mix as seen in table B.5. It was decided to prepare sixteen mixes with an increasing proportion of SCMs to cover a wide range of mixes cast in the Netherlands. In total nine mixes were cast with GGBFS content ranging from 10% to 90% with a step of 10% and four mixes were cast with FA content varying from 10% to 40% with a step of 10%.

The overall mixes design can be found in the table B.5. The chemical composition of the compounds used to design concrete mixes was determined using a desktop-XRF. The results can be found in the table 3.3.

Oxides	CEM I	GGBFS	FA	Crushed fine aggregates	Crushed coarse aggregates
CaO	64.48	37.47	4.39	0.17	0.31
SiO_2	19.97	33.82	55.25	91.07	93.34
Al_2O_3	5.04	14.48	26.25	4.60	3.71
Fe_2O_3	3.44	0.31	6.40	2.36	0.68
MgO	1.88	9.59	1.78	0.5	0.27
K_2O	0.57	0.50	1.43	0.53	0.90
TiO_2	0.37	1.18	1.08	0.18	0.10
P_2O_5	0.43	0.01	1.01	0.11	0.05
Na_2O	0.45	0.47	1.07	0.34	0.51
SO_3	2.95	1.63	0.82	0.02	0.03
Mn_2O_3	0.07	0.28	0.04	0.04	0.00
Cl	0.05	0.03	0.02	0.02	0.02

Table 3.3: Table of the chemical composition of the different powders tested with a desktop-XRF. Reproduced from [12].

3.2 Mix design

The exposure class chosen for the mixes was XC4. The water-cement ratio (w/c) was fixed for all mixes to 0,5. This value complies with the European Standard NEN-EN 206 XC4. The consistency class was selected with a slump of 100 mm to 150 mm according to NEN-EN 8005. Therefore, the water content is equal to 180 $kg \cdot m^{-3}$ for 0/32 mm aggregates, 190 $kg \cdot m^{-3}$ for 0/16 mm aggregates, and 200 $kg \cdot m^{-3}$ for 0/8 mm aggregates. The volume of air was considered to occupy 1% of the total concrete volume.

Special attention should be paid to the mix of cementitious materials during experiments in order to get representative results. As mentioned in the previous part, CEM I 42.5N cement and SCMs were mixed in different proportions. Dur-

ing the casting session, the cement and SCMs were mixed in a sealed bucket for one minute before mixing with aggregates in the concrete mixer. The amount of SCMs required was determined by calculating the volume of cement replaced by SCMs and multiplying this volume by the density of the SCMs. The density for each component is given in the table B.4.

Example calculation of blended SCMs mix design, 10% slag:

Water content: W = 190 kg.m⁻³ Cement content: $\frac{W}{C} = 0.5 \Rightarrow C = 2 \times W = 380 kg.m^{-3}$ Volume of concrete = $15L = 0.015m^3 \Rightarrow V_C = \frac{0.015 \times 380}{3150} = 0.0018m^3$ $m_{slag} = 0.1 \times V_C \times 2900 = 0.525kg$

The mass of compounds in each mix can be found in the appendix table B.5. Materials were put in the concrete mixer in the following order: coarse aggregates, fine aggregates, cementitious materials, and water. All the compounds were mixed for 2 to 3 minutes, depending on the workability of the mixture. There are no standards for mixing time, and the measure of appreciation remains with the experienced technician.

The moulds used were cubes and prisms. Cubes have a dimension of 150 mm, while prisms have a dimension of $400 \times 100 \times 100 \text{ mm}^3$. Prisms were used for mixes with varying aggregate gradation, while cubes were used for mixes with various SCMs content. The moulds were oiled prior to casting. This oil layer prevents the paste from sticking to the mould. The moulds were placed on a vibrating table and poured into two layers. Upon being half and filled, they were compacted. This step removes air entrapped in the mixture. The fresh surface of the concrete was evened using a straightedge.

Next, a plastic sheet was applied to the cast surface to avoid evaporation. The cubes were left for 24 hours at room temperature. Then, they were demoulded, wrapped in plastic film, and put in the curing room at 96% of relative humidity (RH) and 24°C. It was decided to wrap them in plastic film to prevent surface carbonation ¹. The decision to place them in the curing chamber was determined by the temperature and the fact that a moisture-saturated environment slows down the surface carbonation process. This choice can be criticized. The plastic film used in this thesis lets moisture get through and does not support months of exposure to water. The consequence was the appearance of calcium carbonate crystals on the surface of the cube, as well as an uncontrolled moisture content. The cubes used to test reproducibility were cured in another room with a relative humidity of 55% and a temperature of 20°C. They were twice wrapped in plastic film and taped. The concrete cubes and beams were left to cure in the curing chamber for at least 28 days.

¹surface carbonation: process caused by surface leaching of Ca^{2+} and subsequent reaction with CO_2 from the air. Surface carbonation results in the formation of $CaCO_3$

Pictures of the different setups used to seal the cubes can be found in the appendix C.2.

3.3 Methods

This part will detail the two main techniques used during this thesis: hXRF and ESEM-EDS. The first step will be to briefly explain each instrument, along with a table containing more information about each technique. Then, a deeper explanation of the physical principle behind these two techniques will be given in section 3.3.3.

3.3.1 Bruker S1 Titan 800 hXRF

The hXRF used for this thesis is a Bruker S1 Titan 800 handheld Energy Dispersive X-ray Fluorescence analyser. It is equipped with a rhodium tube. This X-ray tube shoots X-rays at an angle of 45° from the center of the analysis tip.

The power of this beam varies from 5 up to 50 kV and can be shot for 10 to 300 seconds. The laser beam is a circle with a diameter of 5 mm. Therefore, the analysis area of the hXRF is approximately equal to 20 mm². This hXRF is equipped with a high-resolution Silicon Drift Detector (SDD) with a resolution of 145 eV. The SDD possesses a graphene window allowing fast and precise analysis. A thin plastic film protects the detector and X-ray tube to avoid direct contact with materials. Five different filters can be added to detect some elements with higher accuracy. However, previ-



Figure 3.3: Bruker S1 Titan X-ray analyser

ous studies that used this equipment revealed that the use of filters gave poor results on concrete [58].

3.3.2 ESEM-EDS

The SEM-EDS used in this thesis is an ESEM-EDS. The difference is the use of moisture by the latter to deal with the electronegativity issue (see 2.2.1). The EDS is a Thermo Fischer^{*TM*} Ultradry EDS detector. The energy of the beam shot with the ESEM ranges from 6 to 50 kV. The beam size equals 125 μm and the area under analysis can be decreased up to 100 mm² by lowering the magnification. The test can be conducted in a vacuum, which is not the case with the hXRF. Furthermore, its windowless SDD allows it to detect lighter elements (up to Be) with a higher resolution (129 eV). The measurement time can take a few

minutes, depending on the desired precision.

The main properties of the two techniques can be found in table 3.4.

Table 3.4: Table comparing the main properties between the hXRF and the ESEM-EDS techniques.

	Energy Dispersive X-ray Spectrometry	handheld X-ray Fluorescence
Туре	Thermo Scientific TM UltraDry EDS Detector	Bruker S1 TITAN 800 hXRF
Range of detectable elements	up to Be	Mg - U
Mechanism	X-Ray Fluorescence	X-Ray Fluorescence
X-ray source	none	Rh-target X-ray tube
X-ray beam path	Vacuum	Air
X-ray beam spot size	150 µm	5 mm
Power	4W (6-50 kV, 5-200µA)	5 - 50 kV
Resolution	129 eV	<145 eV
Sample type	Solid, powder, liquid	Solid, powder
Sample preparation	drying and cleaning	no preparation
Working distance	10 mm	Contact measurement
Active area	up to 100 mm ²	20 mm^2
Acquisition time	few minutes	10 - 300 seconds
Detector	Windowless SDD	Graphene window SDD
Counts per seconds	>1.10 ⁶	$45 \cdot 10^4$

3.3.3 X-Ray Fluorescence

X-ray fluorescence is a non-destructive element analysis technique using X-rays. X-rays are electromagnetic radiation generated by high-energy particles bombarding atoms [34].

Working principle

An atom is composed of a nucleus and electrons which gravitate on different shells as depicted in Figure 3.4. The partially filled shell is called the outer shell, and all the others are called the inner shell. Ionization energy corresponds to the minimum energy required to remove an electron from an atom.

The X-ray fluorescence principle involves shooting X-rays at a sample to cause the element inside the sample to emit secondary X-rays. Therefore, an incident X-ray beam with an energy equivalent to or higher than twice the emission line energy of the heaviest element is shot at the sample [55]. The interaction between the photons in the X-ray and the atoms will lead to the emission of characteristic and continuous X-rays.

The characteristic X-rays will give peaks corresponding to the elements present in the sample. The detection of continuous X-rays will result in the formation of some background noise in the spectrum. These two types of X-rays will be generated by three different modes of interaction inside the sample. The photoelectric interaction, the elastic scattering, also called Rayleigh scattering, and finally, the inelastic scattering or Compton scattering [60]. Photoelectric scattering produces characteristic X-rays. Rayleigh and Compton scattering produce continuous Xrays.



Figure 3.4: Emission of characteristic X-rays. Reproduced from [59]

Characteristic X-Rays

Characteristic X-rays are produced by photoelectric scattering. In this situation, the energy of the photon is fully converted during the interaction with an electron. A part of the energy is used to remove the electron from its shell and to turn it into a free electron circulating inside the sample while the rest is stored inside this electron as kinetic energy [60]. Another electron from a higher shell fills the hole and emits at the same time a fluorescent X-ray as shown in Figure 3.4. The emission of a characteristic photon corresponds to the release of a part of the energy contained in the electron from a higher shell during its transition to the lower shell. This energy will be distinct and corresponds to the difference in energy between the two shells.

Continuous X-Rays

Continuous X-rays result from an interaction between two different elementary particles or groups of particles (electron, photon, or nucleus). The fluorescent X-rays resulting from these interactions will form a continuous spectrum on the background of the hXRF curve.

Elastic scattering, also called Rayleigh scattering corresponds to the elastic collision of a photon with a firmly bound electron belonging to an atom [60]. During this interaction, the incident photon does not lose



Figure 3.5: Photon scattering

energy, its wavelength stays identical, but its trajectory might be changed [61], as depicted in Figure 3.5.

In the case of Compton scattering, the bond of the electron to the nucleus is loose. The scattering will then be inelastic. Inelastic scattering means the photon will lose some of its original energy and be deviated after the impact [60]. As a result, an X-ray with an energy equal to the difference between the original energy of the photon and what was left after scattering will be emitted.

An important effect to mention is the enhancement factor. This effect impacts the detection of lighter elements . The enhancement factor is the effect behind the absorption of secondary X-rays in the matrix of the sample, water, and air.

Enhancement factor (Secondary fluorescence)

Enhancement effect, also called secondary fluorescence, occurs when an element absorbs a secondary X-ray from another element. Suppose a case where two elements with different atomic numbers are located next to each other. The binding energy of the electron in element 1 would be higher than the binding energy of the electron in element 2. Initially, an X-ray with energy superior to the binding energy of element 1 is shot with a device on the sample (step 1). This X-ray will enter the sample and interact with an electron from element 1 (step 1 in Figure 3.6). The electron will be ejected from its shell and emit a characteristic X-ray. This characteristic X-ray could then interact with an electron from element 2 (step 2). This electron would then be ejected as the binding energy of the electron is lower than the energy of the characteristic X-ray. This interaction between the electron and photon would again be a photoelectric interaction leading to the emission of another characteristic X-ray (step 3). However, the energy of this characteristic X-ray would be associated with element 2. Therefore, element 2 will be detected by the hXRF rather than element 1.



Figure 3.6: Enhancement effect between two different elements

3.4 Calibration

Calibration transforms the count rate for each element into a weight percentage for the associated oxide. Each material requires a particular calibration due to their chemical composition and matrix differences. The model for each calibration is trained by measuring the chemical composition of many certified reference materials with a known chemical composition. The count rate of each element is based on the weight percentage of the corresponding oxide. Only the oxides detected in the standard sample used for calibration will be detected in the associated mode. The BrukerTM calibration for cement mode is based on samples with a similar chemical composition to the analysed sample. Cement mode only detects the following oxides: MgO, CaO, Al_2O_3 , SiO_2 , P_2O_5 , SO_3 , K_2O , TiO_2 , MnO, Fe_2O_3 .

3.5 Setup to compare results between hXRF and ESEM-EDS measurements

3.5.1 3D printed moulds

One of this thesis main issues was enabling comparison between ESEM-EDS and hXRF results. It was crucial to make sure that the area analysed by both techniques was optimized because concrete is a highly heterogeneous material. The steps and tools used for this purpose will be explained in this part.

In addition, the surface of concrete might get affected by the environment and its chemical composition might change due to surface carbonation. One of the main factors for surface carbonation to occur is the presence of moisture in the concrete. This latter point was difficult to avoid since cutting was done in a wet condition.

Thus, the time between the two sets of measurements done with the hXRF and the ESEM-EDS was shortened as much as possible to prevent variation in chemical composition at the surface of the sample due to surface carbonation. The tests with the hXRF and preparation of the samples for ESEM-EDS were conducted in approximately 9 hours. These samples were stored in a climate chamber and tested under ESEM-EDS.

First, 3D printed pieces were designed to draw the square shape on the top of the concrete surface. The 3D mould designed to draw the square is represented in Figure 3.7.



Figure 3.7: Mould for drawing the 9 squares on the concrete surface.

These squares were cut to fit in the ESEM-EDS chamber. This equipment cannot accommodate samples larger than 50 mm \times 50 mm. The sample size has even been reduced to 25 mm \times 25 mm to fit four samples in the ESEM-EDS. The cutting session will be explained in subsection 3.5.2. A length of 5 mm distanced each point to avoid overlap between the measurements. The points were also separated by a distance of 5 mm from the cutting lines. This is done to ensure that no surface measured by the hXRF gets damaged during the cutting stage. All areas less than 3.75 cm from the sides were discarded. Those constraints resulted in producing nine samples of 25 mm \times 25 mm with four measurement points each. Concrete surface labeling can be seen in Figure 3.8.



Figure 3.8: Point acquisition on the concrete surface.

Another plastic mould was designed to locate each of the four points on the

squares. This mould was 25 mm \times 25 mm with four square holes. The four squares have equal dimensions and correspond to the size of the area analysed by ESEM-EDS. On the one hand, the X-ray beam of the hXRF is a disc with a diameter of 5 mm. On the other hand, the size of the analysed area can be modified for ESEM-EDS. Increasing the area under analysis can be done by changing the magnification. At one hundred times magnification, the area examined is a rectangle of 4.131 mm by 2.757 mm. Under lower magnification, the area around the center of the picture analysed appears blurry. The bluriness of the image is a sign that the detection of X-rays coming out of the sample is not optimal. Thus, the magnification of one hundred times is the most appropriate compromise between a large area and the quality of the results. The holes inside the plastic mould were slightly extended to include the mark of the carbon pen. The dimensions of the holes inside the plastic moulds were extended to 4.9 $mm \times 3.5 mm$. The choice to use a carbon pen to draw the lines on the samples was motivated by the impossibility of detecting carbon with hXRF and the possibility of avoiding its detection with ESEM-EDS. The plastic mould and the square observed under the ESEM-EDS can be seen in Figure 3.9. The carbon appears darker on the top left and the bottom right of Figure 3.9b.



(a) plastic mould used to draw the delimitation of the area analysed by the ESEM-EDS.



(b) Picture done with the SEM of the area with the carbon mark.

Figure 3.9: Plastic mould used to draw the contour of the area for ESEM-EDS and observation of the area under ESEM-EDS.

A picture of the samples after the cutting and marking stage is depicted in appendix C.5.

The most difficult aspect of the hXRF was to ensure that the beam spot was placed at the right location on the surface. In addition, it was imperative to ensure that this process was reproducible on each cube. The tip of the hXRF is large, and it was impossible to 3D-print a single plastic mould per surface. Thus, six different pieces of plastic were created to test 36 points per surface.

The pieces are in a U-shape. A hole is located in the center of the item to position the hXRF tip during measurement. This hole has a size of 17 mm \times 75 mm. The overall dimension of the central part is 160 mm \times 50 mm. The thickness of the central part is equal to 1 mm. The top of the metallic part is slightly thicker, allowing it to fit in the mould while being in contact with the concrete surface, as seen in Figure 3.10. The two lateral parts exist to hold the central part. Their width is identical to the central part, but their thickness is equal to 5 mm, and their length is equal to 50 mm.





(a) Diagram of the plastic mould to hold the hXRF.

(b) Picture of the mould on top of the hXRF.

Figure 3.10: Modelisation and picture of the plastic mould piece created to fit the hXRF during measurements.

The position of the hole placed on the central component changes through the length to fit the list of points on the surface. The distance between the top of the metallic item on the tip and the center of the beam spot is equal to 24.5 mm. This distance can be seen in Figure 3.10a. The testing points are located at 45 mm, 55 mm, 70 mm, 80 mm, 95 mm, and 105 mm on the surface (see Figure 3.8). So, the hole in the central item was placed at 20.5 mm, 30.5 mm, 45.5 mm, 55.5 mm, 70.5 mm, and 80.5 mm. This length is labeled x1 on the drawing of the plastic mould in Figure 3.10. An extra 5 mm was added to these previous values to account for the thickness of the lateral part. The red dot corresponds to the location of the beam emitted out of the hXRF. Figure C.6 shows the group of six moulds.

The samples were labeled before the cutting session. The number of the surface was written in the top left corner (numbers ranging from I to III) and the number of the sample was written in the bottom right corner (numbers ranging from 1 to 9). This labeling was done to track the sample prior to ESEM-EDS measurements. The labeling of the samples is depicted with green numbers in Figure 3.11.

The samples were analysed with the ESEM-EDS after measuring the concrete with the hXRF and cutting the sample. The order in which both sets of measurements were done does not correspond. The reason for this mismatch is the separation of the surface into nine samples. The numbers associated with the ESEM-EDS and hXRF measurements are represented in Figure 3.11. The numbers associated with the ESEM-EDS measurements appear in blue, and the ones done with the hXRF appear in pink. The ESEM-EDS measurements in the excel sheet were modified to match the measurements done with the hXRF.



Figure 3.11: Number associated to the hXRF and ESEM-EDS results for points 1 to 36.

3.5.2 Cutting the samples for EDS measurements

The surfaces were cut after drawing the measurement pattern on the concrete cube and taking the measurements with the hXRF. Two different saws were used. Both can be seen in Figure 3.12. The smaller saw has higher precision as well as a thinner blade.



(a) Saw used to cut the cube



(b) Saw used to cut the surfaces

Figure 3.12: Saws used for preparing ESEM-EDS samples.

The first blade thickness is approximately 4 mm. The second one has a thickness of 3 mm. First, the whole surface was cut with the larger cutting machine depicted in Figure 3.12a.

The thickness was calculated to be approximately 2 cm, as represented in the Figure C.3. Then, the nine squares were cut with the help of the smaller saw represented in Figure 3.12b. Both cutting sessions were done in wet conditions for safety reasons. Dry cutting results in a lot of dust being released into the air.

After being cut, the samples were placed in aluminum trays, as seen in Figure C.7. Those trays were placed in a Nuve TK120 climate chamber shown in Figure 3.13. They were dried at 60°C and 0% Relative Humidity (RH). The RH was set to 0% to limit surface carbonation.



Figure 3.13: Climate chamber Nuve TK120

3.6 Tests to determine the influential factors on hXRF measurements

3.6.1 Impact of the sample edges

Introduction

The volume of interaction between the beam and the sample has a pear shape due to the scattering of photons. It might result in the dissipation of some X-rays in the case of a measurement done next to the edge of the sample. The X-rays gravitating around the perimeter of the pear shape would then leave the sample and get dissipated in the surrounding environment. This loss of information might result in a change in the weight percentage of each oxide calculated after normalization.

Method

Before testing, the sample was wrapped and left to cure for 37 days in the curing room. On the first day, the sample was tested twice on two separate surfaces 5 mm from the edges. The chemical composition of the sample was measured along the length of the cube every 5 mm. The first set of measurements was judged non-representative after analysis due to a lack of practice and the necessity to warm up the X-ray tube prior to measurements. On the second day, a professional from the Institute of Reactor Physics and Nuclear Materials at TU Delft verified the amount of radiation emitted by the hXRF during the experiments.

3.6.2 Measurement time

Method

The chemical composition of the cube was first measured several times on the same point for various times (from 10 up to 180 seconds with a step of 10 seconds). This first set of measurements was done to see if increasing the measurement time for one point would increase the precision of the results. Then, the study was extended to examine the impact of time on many points. Previous studies done on soil samples predicted that the optimum time would be 60 seconds [62]. However, studies led on concrete by Yundakul et al. [63] estimated that the optimum time was 30 seconds. Based on these two studies, it was decided to study the impact of the time for 10, 20, 30, and 60 seconds on 60 measurements. On the first day, the impact of the time was only studied for 10, 20, 30 seconds. Then, on the second day, the impact of the time was studied for 30 and 60 seconds. Results were obtained from two different cubes.

3.6.3 Acquisition pattern

Method

The first measurements on concrete revealed that factors such as surface carbonation could give different results from measurement to measurement. A solution to this issue could be to take many measurements [64]. The choice to measure the chemical composition on various points raises the question of how to perform measurements. Only two possible patterns exist: the regular pattern and the random pattern. Human choice cannot be random. Therefore, a code was then written to avoid biases when choosing randomly generated values. Eight different regular patterns were created, as presented in Figure 3.14. Each random and regular pattern has the same associated number of points (n = 12, 15, 27, 29, 36, 48, 54, 72). Bell curves were plotted to compare the two different patterns using the averages and standard deviation (SD). The number of points associated with each was chosen as widely as possible to study the impact of the number of points on the results.



Figure 3.14: Design of the regular patterns.

Normal distribution curve

A normal distribution curve or bell curve represents the accuracy and precision of a set of measurements. The density of probability is represented on the Y-axis. The density of probability corresponds to the chance of getting the point corresponding to the x-value. The values on the Y-axis are obtained from the values on the X-axis using the equation 3.3.

$$y = \frac{100\%}{\sqrt{2 \times \pi}} \times e^{-\frac{x^2}{2}}$$
(3.3)

The median and the mean of the values are superposed and can be found in the middle of the curve. The number of values at 1, 2, and 3 standard deviations (SD) from the mean is always identical. Approximately 68% of the values are contained in the ± 1 SD, 95% of the values at ± 2 SD, and around 99% at ± 3 SD.

3.6.4 Moisture impact and number of points

Introduction

The paste contains hydration products, unreacted cement, pore solution, capillary and gel pores. Pores might be connected and form a pore network, or they can be separated from the rest as isolated pores. Two type of pores exist: gel pores and capillary pores. The size of gel pores will be approximately ten times smaller than capillary pores (around 2-3 nm in the nominal section). Thus, most of the interaction between the external environment and the porous system will occur through the capillary pores.

Due to their size and shape, pores tend to attract moisture until an equilibrium point is reached between the inner and outer environment. At the same time, moisture inside the pores will condensate due to a difference in pressure, turning into water. This water contained in concrete will have a higher impact than air on the secondary X-rays emitted by the sample. The density of water is higher than air, meaning that water molecules will intercept more X-rays. Lightweight elements are more sensitive to this effect due to their longer wavelength X-rays compared to heavier elements. Depending on the equipment and sample analysed, lightweight elements are defined differently. Figure 3.15 shows the absorption of X-rays by water.



Figure 3.15: Graphic representing the absorption of X-rays by water.

Method

First, the tests were done on a dried cube, and then the cube was wet and tested again. The process was done in this order to decrease the time lapse between the two tests. The decrease in time between the two measurements limits the surface carbonation process.

The cube was initially placed in a climate chamber, represented in Figure 3.13, at 60°C with a 0% relative humidity (RH). Then the cube was weighed every 24 hours to evaluate the weight change. The cube was considered dried when the weight change became negligible. The cube stayed for 14 days in the climate chamber before being tested. Afterward, its chemical composition was measured 108 times. The measurement period for each point is 30 seconds at a power of 15 kV. Every six measurements, the surface was wetted. The surface was wetted with a soaked cloth. After this, excess water was swept off the concrete surface with a dry cloth. No free water must be left on the surface to avoid damaging the hXRF detector.

3.6.5 Surface carbonation

Introduction

Carbonation is a process in which CO_2 diffuses inside concrete pores and dissolves in the pore solution. Due to the reaction occurring in the region near pores, the carbonation rate will vary depending on the surface morphology. There are two paths for the dissolution of CO_2 depending on the PH of the environment. Dissolution of CO_2 will be obtained by the hydroxylation of carbon dioxide and the hydration of CO_2 . The hydration of carbon dioxide in water will result in the formation of carbonic acid (H_2CO_3). Carbonic acid will then give two protons in a two-stage process to generate carbonate ion (CO_3^{2-}). In the case of hydroxylation, CO_2 will be in contact with hydroxide ions present in the pore solution. This will result in the formation of bicarbonate ions (HCO_3^{-} . Bicarbonate ions will then combine with hydroxide ions to form carbonate ions (CO_3^{2-}). Those carbonate ions will react with calcium ions (Ca^{2+}) in the pore solution to produce calcium carbonate.

Method

This study aimed to avoid surface carbonation rather than quantify its effect as quantifying the carbonation effect with hXRF is difficult. Surface carbonation was observed during this thesis due to improper curing condition as explained in section 4.1.1. Therefore, it was pertinent to understand the impact of surface carbonation on concrete. The impact of carbonation was studied by doing two sets of measurements on two cubes with different exposure times to air. The first cube was moved out of the curing chamber after 44 days. Then it was left outside for 8 hours. Subsequently, it was placed back in the curing room for a week and then tested. The second cube was directly tested after being taken out of the curing room. This cube stayed in the curing room for 51 days.



Figure 3.19 illustrates the time frame of both testing sessions.

Figure 3.16: Time frame for the surface carbonation of samples.

3.6.6 Presence of aggregates at the surface

Introduction

The amount of silica detected by the hXRF on CEM I-based concrete exceeds the value measured with ESEM-EDS by 4%.

The two factors possibly impacting the weight percentage of silica in this thesis are surface carbonation and the presence of aggregates on the surface. Carbonation would result in a decrease in the SiO_2 content. Consequently, only the presence of aggregates can be considered to increase SiO_2 content. Aggregates represent $\frac{3}{4}$ of the total volume of materials found in concrete. As shown in the table 3.3, powders made of crushed fine and coarse aggregates contain at least 91% of SiO_2 . CEM I cement contains only 20% of SiO_2 . Consequently, the presence of aggregates at the surface would increase considerably the amount of SiO_2 in the final results.



Figure 3.17: Impact of the small particles on the particle size distribution. Adopted from [65].

The wall effect can explain the presence of aggregates at the surface. The wall effect is caused by the edge of the mould. It results in the formation of a random forced packing of particles on the surfaces of the cube. The depth of this peculiar packing is between one and ten particle size [65]. The surface of the cube contains a larger amount of smaller particles.

The cohesive forces dominate the packing between smaller particles. These aggregates will tend to agglomerate and repulse coarser aggregates as seen in Figure 3.17. This is the case for particles with a diameter smaller than 1mm. These particles represent almost 33% of all the particles in the 0-16 mm mixes as observed in the table B.3. Therefore, the presence of aggregates on concrete surfaces is expected.

Method

Pictures were obtained with a digital microscope to investigate the presence of aggregates on the surface. Concrete has a bumpy surface. Stitching the pictures in 3D is, therefore, necessary. 3D stitching implies that the digital microscope will take many pictures of the same area at different heights with a defined gap between them. It will process the data and generate a high-definition composite image from all the pictures. These pictures were obtained with a magnification of $300 \times$ and a gap of $10 \ \mu m$. Twenty pictures were used to determine the paste over aggregate ratio $(\frac{P}{A})$. The stitching raised the question of the overlapping of aggregates by paste.

Mapping of 4 surfaces with the ESEM-EDS was done to identify the area rich in silica corresponding to the aggregates. The 3D pictures and mapping were compared to determine if paste covered aggregates. Finally, pictures were processed with the use of JMicrovision to determine the $\frac{P}{A}$ ratio. A total of 250 points were set one by one in a random pattern on the picture by the software. The user can determine whether the points were placed on aggregates, voids or paste.

3.7 Code

Codes were written to import the Excel data obtained with the hXRF and ESEM-EDS. Data were extracted from these excel sheets and manipulated to draw the different curves and calculate the ratios. Most of the codes were written following the same outline. Only the most important parts of the codes will be discussed in this section.

3.7.1 Code to randomize the choice of values

A random selection code was necessary to compare the regular and random patterns. The hXRF results are contained in an Excel sheet. Each of the lines has an associated number. A vector containing random values with values ranging from 0 up to the number of lines in the Excel sheet was created. Each of these values corresponded to one of the lines in the Excel sheet. Ensuring that all the numbers differed was imperative to avoid duplicate values in the newly created Excel sheet. Then, each of the lines drawn randomly would be extracted and placed in another table. The part of the code needed to generate the random vector r can be found in Figure 3.18.



Figure 3.18: Code to create the vector r containing random values.

An endless loop was created to ensure that the random vector r would have a size equal to m_max. Then, a random value between 0 and m_max will be associated with the num value. This value will be compared to see if it is already present in the vector r. If it is, the code returns to the beginning of the loop while choosing another random number num. If the value is not already contained in r, the code fills the box at row i1 with the value num. Then it increments the vector count and starts again in the loop 'for'.

3.7.2 Code to read and modify Excel sheets



Figure 3.19: Code to read and modify the tables in the Excel sheets.

First, a loop is created to repeat the same action for each file containing measurements from experimental experiences. The program reads the Excel sheet containing all the measurements in this loop. This table is stored in the data named 'load'.
Then, it creates a new Excel sheet to store the data extracted from 'load'. Rows of the file 'load' will be selected according to the list of random values contained in the table r (see section 3.7.1) and uploaded in the new file named 'repro1.csv'.

Chapter 4

Results

4.1 Factors impacting the measurements

hXRF is a technique requiring no sample preparation. Nevertheless, this advantage will also result in a decrease in accuracy and precision. Thus, some external factors will impact the measurements. Prior studies already determined some of these factors: time [66], moisture [67, 68], matrix effect [64, 67, 68]. Another significant factor impacting the results is the surface carbonation of concrete due to the formation of calcium carbonate at the surface.

No prior study was conducted to determine the impact of these factors on concrete. Therefore, these factors were observed after impacting the first measurements subsection 4.1.1. All the studies on the factors impacting the measurements were done on CEM I-based concrete. Its chemical composition is better known than most of the other mixes.

As no previous data was obtained with the hXRF on concrete, results were compared to those obtained with the ESEM-EDS. These values were considered to be the true value. The controlled environment in the ESEM-EDS motivated this choice. Therefore, the ESEM-EDS values determined the actions in the protocol.

4.1.1 Impact of the sample edges

Figure 4.1 represents the weight percentage of each element through the length of the cube. Each point corresponds to a measurement. Only the curve corresponding to calcium will be discussed here for clarity. The curve is represented in Figure 4.1. The X-axis represents the distance of the measurements to the edge of the cube. The Y-axis represents the weight percentage of the calcium oxide. The appendix C.8 contains the other curves. The cube was tested on three different surfaces over two days. On the first day, the chemical composition of the concrete cube was assessed on two different surfaces. On the second day, one of the surfaces was tested again, and a third surface was tested.

On the second day, an expert from the Reactor Institute Delft at TU Delft monitored the measurements. His presence was essential to ensure the safety of the users during the measurements. The expert used a dosimeter to identify radiations coming out of the sample. Measurements done 2.5 cm from the edges proved that no X-rays escaped the concrete. However, few X-rays escape concrete when measurements are closer to the edge. The technician explained that these X-rays were not harmful in such a small quantity. Nevertheless, to avoid any risk, it was decided to take all measurements at least 2.5 cm away from the sides.



Figure 4.1: Evolution of the *CaO* content across the length of the concrete surface.

The green curve corresponds to the first test on a concrete surface (surface 1) with the hXRF. The black and blue curves correspond to the measurements on surface 2 done on two consecutive days. The red curve corresponds to measurements done on a third surface during the second day. The first test was done as a test with the plastic moulds represented in Figure 3.10. Thus, the results represented on the green curve are highly inaccurate and difficult to explain. Measurements fluctuated significantly compared to the other measurements, as seen with the 1 SD area in Figure 4.2. Therefore, observations will not be done based on the green curves. The four sets of measurements were also plotted using bell curves as represented on Figure 4.2. The Y-axis on the bell curve represents the probability density, and the X-axis represents the values corresponding to the probability density. The points on the bell curves represent the measurements, the dotted lines represents the first standard deviation area.

In the first place, the bell curves indicate that the technique is reliable. The 1SD area concentrates most of the points. These measurements were done without considering any of the factors impacting them. Thus, the SD appears small. Furthermore, the second test on surface 1 was due to the 5th point between 20 and 40 mm in Figure 4.1 Calcium content is locally higher than the average, whereas the SiO_2 and SO_3 content has decreased. The blue curve corresponding to the measurements done the second day on the same position follows the same trend. The rise in calcium is probably due to localized carbonation on the concrete surface. This point shows that results will be identical if a measurement is done twice at the same point. In addition, the average of the blue and red bell curves almost overlaps. Those two curves correspond to the test of two surfaces on the second day. It means that measuring 24 points on the same cube gives reproducible results.



Figure 4.2: Bell curve of the measurements done through the length of the cube.

However, the precision between the two sets of measurements changes. A more precise set of values means more values will be close to the average. At the same time, the probability of finding a value in the neighborhood of the average increases. Hence, a narrower and higher curve indicates a more precise set of measurements. The maximum of the blue curve is higher than the maximum of the red curve. The values are less spread in the case of the blue curve. The smaller SD of the blue curve confirms this observation. Therefore, the measurements on surface 2 on day 2 (blue curve) are more precise than those on surface 1 (red curve). The difference in the matrix on the two surfaces and the local carbonation explain this difference in precision.

Unpredicted factors impacted the first measurements. Their impact can be noticed while comparing the red and black curves. The average calcium content for the measurements done on day 2 (red curve) is higher. This higher calcium content could be due to moisture or surface carbonation. Cubes were taken out of the curing room in wet condition. They were left out during the test and sealed before tests led on day 2. Thus, the moisture content in this cube could only be lower on day 2. A decrease in moisture content results in a lower value for *CaO* as explained in section 4.1.4. Therefore, the increase in *CaO* content increase while SO_3 and SiO_2 content decreases for the black curve. The same behavior is observed with surface carbonation in section 4.1.5. Therefore, this difference in *CaO* content is due to formation of calcium carbonate at the surface.

Finally, SiO_2 content is higher than expected. The weight percentage exceeds the value obtained from the measurements done with the ESEM-EDSDS by 3 to 5%. This rise could be due to the presence of aggregates on the concrete surface. This increase of SiO_2 content would also explain the decrease in the weight percentage of CaO between ESEM-EDS and hXRF measurements.

4.1.2 Measurement time

Measurement time, also called analysis time, corresponds to the exposure time to X-rays. Figure 4.3a represents the first set of measurements. The blue curve corresponds to the measurements with an analysis time of 30 seconds. The green curve to a measurement time of 20 seconds, and the red curve to a measurement time of 10 seconds. Figure 4.3b represents the second set of measurements. The orange curve corresponds to the measurements done with an analysis time of 30 seconds, and the pink curve corresponds to the measurement with an analysis time of 60 seconds. Qualitative analysis is done on the curve before performing a quantitative analysis using Relative Standard Deviation (RSD). Appendix C.10 and appendix C.12 contains the rest of the curves. First, the curves have identical shapes. The fact that they have identical shapes indicates that they converge at the same rate. These curves have similar precision if they converge at an analogous rate.

Nevertheless, the three sets of curves differ in terms of accuracy. The last value symbolizes the accuracy of the set of measurements. The curves should overlap if they have the same accuracy. However, they end up in different positions. Therefore, the accuracy evolves with the measurement time. No change in the accuracy and precision occurs between the analysis time of 30 and 60 seconds as the curves overlap. The overlap of the two curves implies that no gain in accuracy is obtained for measurement time above 30 seconds. Thus, the optimum analysis time for concrete is 30 seconds based on the qualitative analysis.



Weight percentage of the oxide CaO 62.0 weight percentage (%) 61.5 61.0 60.5 60.0 30 seconds 59.5 t = 60 seconds 60 10 20 30 40 50 number of measurements

(a) Diagram of the weight percentage as a function of the number of points for 10, 20, 30 seconds

(b) Diagram of the weight percentage as a function of the number of points for 30, 60 seconds.

Figure 4.3: Diagram of the weight percentage as a function of the number of points for various times.

The RSD measures the precision of replicate results between two different techniques. Measurements obtained with the hXRF and the ESEM-EDS are compared. The precision varies for each element. The quality of the results can be divided into three different categories as shown in the table 4.1:

Table 4.1: Table of the data quality criteria in terms of precision [69].

Q3 (definitive)	RSD < 10%	Identical precision, $y = x$
Q2 (Quantitative Screening)	RSD <i>c</i> [10%,20%[Linear correlation between the precision of both techniques $y = mx$ or $y = mx + c$
Q1 (Qualitative screening)	RSD > 20%	No possible correlation

The table 4.2 contains the values of the RSD for the average of 60 measurements for a measurement time of 10, 20, 30, 30^{* 1}, 60 seconds. Furthermore, the RSD is inversely proportional to the number of counts as seen in the equation 4.1 from [69]. This result means a larger number of counts will lead to a smaller RSD and higher precision.

$$\% RSD = \frac{100}{\sqrt{number of counts}} \tag{4.1}$$

First, elements in a higher concentration have a reduced RSD. *CaO*, which is the main oxide in CEM I 42.5N cement (approximately 64%), has the lowest RSD, while *MnO*, with a concentration of less than 0.02%, has the largest RSD.

¹Two sets of measurements were done with an analysis time of 30 seconds

Its RSD is approximately ten times wider than the one for *CaO*. In addition, *CaO*, *Al*₂*O*₃ and *Fe*₂*O*₃ have an RSD of less than 10%. These elements are the ones present in higher concentration. The low RSD of these oxides indicates that the results obtained with the hXRF are precise compared to the destructive technique for these elements. The variation in the density of aggregates at the surface might explain the high value for *SiO*₂. Elsewhere, secondary X-rays from lighter elements (elements with an atomic number below 20) are more easily absorbed. Their absorptions result in a decrease in the count rate and an increase in the RSD. The comparison between iron and alumina, or potassium with sulfur proves this point. The RSD for iron (Z = 26) is lower than the RSD for alumina (Z = 16), even if the alumina concentration is higher. Therefore, the precision increases proportionally to the atomic number. These results align with the research done by Parsons et al. on soil samples [69]. Researchers in this article concluded that precision depends on the atomic number and concentration of the elements.

Ovido	RSD (%)							
Oxide	10 seconds	20 seconds	30 seconds	30 seconds ¹	60 seconds			
CaO	4.3	4.41	4.61	4.71	4.79			
SiO ₂	10.81	11.52	12.15	12.55	12.76			
Al_2O_3	8.43	9.44	8.20	9.45	9.01			
Fe_2O_3	6.88	7.16	7.65	8.44	8.40			
MgO	—	_	-	-	-			
TiO_2	19.12	19.19	19.25	20.20	20.26			
P_2O_5	27.44	35.83	29.63	27.51	21.78			
MnO	39.50	41.90	40.08	41.40	40.22			
K_2O	19.97	19.48	19.17	25.65	25.01			
SO_3	25.75	22.52	21.78	21.09	21.33			

Table 4.2: Table of the relative standard deviation for the different oxides as a function of the time for 60 points.

Finally, the results show that a higher time does not lead to higher precision. The RSD increases slightly with prolonged analysis time for the following oxides: CaO, SiO_2 , Fe_2O_3 , and TiO_2 . The RSD decreases at higher measurement time for those oxides: K_2O , SO_3 , Al_2O_3 . The rest of the oxides do not show a constant increase or decrease in RSD with increasing analysis time. For t = 10 seconds, 20 seconds, 30 seconds, these changes represent only an insignificant change in most cases of less than 2% except for MnO and SO_3 . Variations of the RSD between 30 and 60 seconds are lower than 1% for all the oxides. Thus, analysis time does not impact precision for measurement time higher than 10 seconds.

Second set of 60 points done with a measurement time of 30 seconds

However, it does not give information on the rate at which precision increases regarding the number of points. The following information is given by Figure 4.4 of the RSD versus the number of points for each measurement time.



Figure 4.4: Curve of the evolution of the relative standard deviation for SiO_2 and CaO.

Precision does increase with analysis time in the case of single measurements on concrete except for Al_2O_3 , MnO, and P_2O_5 . However, measurements with a shorter analysis time have a lower RSD after two measurements. The RSD increases up to the average of 8 measurements and then decreases before stabilizing for an average of approximately 20 points. This trend means that precision will not vary after 20 measurements. Fewer points would result in a loss of precision between results on different cubes, and a higher number of points would be a loss of time concerning precision.

Another important parameter to look at is accuracy. The accuracy was determined by calculating the percentage error of the results. The percentage error represents the difference between the experimental and true values. In the case of this thesis, the true value was set as the average of 60 measurements done with the ESEM-EDS, and the experimental value is the value obtained with an average of 60 points for 10, 20, and 30 seconds. The percentage error values can be found in Table 4.3. The table 4.3 combined with the Figure 4.4 prove that the accuracy of the measurements does increase for a time varying between 10 and 30 seconds. It also proves that 60 seconds will not give more accurate results than 30 seconds. Thus, the measurement time for the guideline is set to 30 seconds.

Ovido	Percentage error (%)						
Oxide	10 seconds	20 seconds	30 seconds	30 seconds	60 seconds		
CaO	5.70	4.60	4.11	4.30	4.64		
SiO ₂	15.51	13.76	12.50	13.29	13.57		
Al_2O_3	12.95	11.05	12.23	17.20	18.47		
Fe_2O_3	30.58	31.74	32.06	30.35	30.08		
MgO	inf	inf	inf	inf	inf		
TiO_2	22.09	20.70	19.23	22.51	23.12		
P_2O_5	30.71	22.73	28.47	34.79	40.91		
MnO	84.65	84.87	84.86	84.17	84.20		
K_2O	69.41	50.78	33.39	61.14	57.68		
SO_3	23.12	17.47	13.58	5.92	6.55		

Table 4.3: Table of the percentage error for the different oxides as a function of the time

4.1.3 Acquisition pattern

The influence of measurement patterns on results was investigated after deciding to take multiple measurements on a cube. In this case, a bell curve plot was preferred because of the ease of analyzing the two patterns. The X-axis corresponds to the weight percentage for each oxide. The Y-axis gives the density of probability. The random pattern appears as the red curve, and the green curve corresponds to the measurements done with a regular pattern. The points are materialized with stars. The approximation of the bell curve is plotted with a dashed line on top of the points. Their respective average was plotted as a vertical line with a color matching their respective curve. The vertical black line corresponds to the average of 108 measurements done with ESEM-EDS at the same position on the cube.

The colored area below the bell curve corresponds to the area between $\pm 1(\sigma)$, $\pm 2\sigma$, and $\pm 3\sigma$. The color opacity decreases for each SD. The scale for each curve varies. The rest of the Figures for the other oxides are in appendix C.14.

The fit between the curves representing the random and regular pattern increases with the number of points. The two curves obtained for 72 points overlap in most of the cases. On the one hand, increasing the number of points means increasing the chance of using the same measurement points out of the list of 108 measurements for the random and regular patterns. Results will then converge to the same value when the number of points selected increases. On the other hand, the average of a higher number of values will be less impacted by the end values.

Elsewhere, values on the y-axis in Figure 4.5b never rise above 0.25, whereas the values on the y-axis in Figure 4.5a increase up to 0.35. The density of probability seems to decrease with the increase in the number of points averaged. The same decrease in values on the y-axis also occurs for the rest of the oxides. A higher number of points will be equivalent to an increase in the chance of getting a more scattered plot due to extreme values. This wider range of values will cause the SD to increase and the density of probability to decrease.

Similarly, density probability increases for elements with a lower concentration. The density of probability will be above 0.35 for CaO (average concentration equal to 60.62% for 12 points) and above 80 for MnO (average concentration equal to 0.077% for 12 points). This difference in the density of probability is because the area below the curve is conserved. A lower concentration will imply a lower SD. This low SD causes an increase in the density of probability, as seen for *MnO*.



(a) Bell curve of CaO oxide for 12 points

(b) Bell curve of CaO oxide for 72 points



(c) Bell curve of Al_2O_3 oxide for 12 points

(d) Bell curve of Al_2O_3 oxide for 72 points

Figure 4.5: Bell curves of the weight percentage obtained with a random and regular pattern for CaO and Al_2O_3 .

The values are closer to the average with the regular pattern. Therefore, the SD of the regular pattern is lower than the SD of the random pattern. The probability of values being close to the average increases simultaneously. Thus, the random curve will have a higher maximum as seen in Figures 4.5a and 4.5c. Despite this, the average of the random pattern is closer to the average of the 108 points calculated with ESEM-EDS. According to table 4.4, the difference between the average for the two patterns and the value obtained with the ESEM-EDS does not seem to decrease with the number of points. Therefore, based on these results, the average of a higher number of measurements does not seem to lead to enhanced accuracy.

Floments	Percentage error (%)							
Elements	12	14	27	29	36	48	54	72
CaO	6.0	5.2	5.4	5.3	6.6	6.2	5.7	6.1
Al_2O_3	18.5	15.9	16.4	16.4	19.9	18.6	17.1	18.1

Table 4.4: Table of the percentage error between the regular and true value.

This part aims to provide results as similar as possible to those obtained with ESEM-EDS. Thus, the criteria to decide which pattern to use for the thesis was based on accuracy rather than precision. The difference between the average of the two patterns is insignificant. The error does not exceed 5% except for P_2O_5 . Thus, both patterns can be chosen. It was decided to use the random pattern since it comes slightly closer to the true value at 72 points except for Fe_2O_3 and the ease of doing calculations with the code. It is interesting to notice that the average of the regular pattern is closer to the true value with an average of 36 points or less in the case of CaO, K_2O , and SiO_2 .

The homogeneity of the aggregate density at the surface of the cube might explain the small deviation of the values in the table 4.5. Similarly, the variation of the SiO_2 content through the length of the surfaces of a cube is small except in the case of carbonation, as seen in Figure 4.1. SiO_2 content will vary with each measurement but the average of multiple measurements will decrease these variations. Homogeneity of the aggregate density over the surface is also shown in appendix C.8. Thus the ratio CaO/SiO_2 stays the same for the eight different patterns when using the regular pattern (see table 4.5).

Table 4.5: Table of the ratio between CaO and SiO_2 for the regular pattern.

	Ratio (-)							
CaO/SiO ₂	12	14	27	29	36	48	54	72
	2.18	2.25	2.23	2.23	2.14	2.17	2.21	2.18

4.1.4 Moisture impact and number of points

The concrete cube was estimated to be dry after 14 days. Theoretically, a cube should be considered dried if its weight is the same for two consecutive days. The difference in weight between a concrete cube stored in a climate chamber for 14 days and a dried cube is equal to 0.73%. Furthermore, four different mixes were tested per week following this protocol. Thus, drying the concrete cube for 14 days was considered a reasonable choice between accuracy and time efficiency, especially when considering concrete surface drying.

The variation in the weight of the cube can be found in table 4.6:

hours	weight (g)	hours	weight (g)
24	7974.8	192	7736.2
48	7860.4	216	7726.9
72	7830.8	240	7718.2
96	7809.4	312	7691.4
168	7746.1	336	7679.9

Table 4.6: Evolution of the weight of the concrete cube in the climate chamber at 60°C and 0% relative humidity.

First, the weight percentage of Al, Si, P, S, and K drops in wet conditions as seen on the curves figs. 4.6a and 4.6b. Secondary X-rays from these elements will interact with the hydrogen and oxygen molecules present in water. Secondary X-rays from lightweight elements will get absorbed through the electrostatic or Compton scattering effect due to the presence of water molecules as explained in section 3.3.3. Due to the loss of energy caused by Compton scattering, the secondary X-rays cannot get detected. The decrease is significant due to the higher density of water compared to air. These effects happen less in the case of a too-high difference between the energy of the secondary X-ray and the binding energy of the electron. Thus, heavier elements are less impacted by this effect.

At the same time, the weight percentage of heavier elements ($Z \ge 20$) increases, as can be seen in the curves figs. 4.6c and 4.6d. Weight percentages are calculated based on stoichiometry. Elements are detected first based on the number of X-rays perceived. Then, the elements are converted into oxides through calibration. The weight percentage of these oxides is then normalized to have a total weight percentage of oxides equal to 100%. If the weight percentage of other oxides will increase. Therefore, the weight percentage of oxides less affected by moisture will increase. This is the case for *CaO*, *Fe*₂*O*₃, *TiO*₂ and *MnO* oxides in this study.



(a) Curve of the moisture impact on SiO_2 (b) Curve of the moisture impact on Al_2O_3



(c) Curve of the moisture impact on Fe_2O_3 (d) Curve of the moisture impact on CaO

Figure 4.6: Impact of the moisture on the weight percentage of Fe_2O_3 , CaO, SiO_2 , Al_2O_3 .

Moreover, the detector did not detect magnesium oxide during the test in wet and dry conditions. The amount of magnesium identified with the ESEM-EDS was equal to 1.74% on average. Under the cement calibration, magnesium oxide will be detected if the amount exceeds the limit of detection (LOD²) of 3000 ppm. The conversion of one ppm in percent gives 0.0001%. So, 3000ppm corresponds to 0.3% of *MgO*. Thus, the hXRF should notice the presence of magnesium oxide in CEM I-based concrete even with the presence of aggregates.

The value corresponding to the average of 108 measurements done with the ESEM-EDS was plotted as an horizontal green line. This part of the thesis aimed to approach the results obtained with the ESEM-EDS. Most of the averages of the 108 measurements done with the hXRF in wet conditions fall closer to the average of the 108 measurements done with the ESEM-EDS. This is the case for the following oxides: *CaO*, *SiO*₂, *Al*₂*O*₃, *SO*₃ and *P*₂*O*₅. Therefore, the measurements of the surface chemical composition should be done in wet conditions.

²Limit of detection (LOD): smallest concentration that can be detected when the sample covers the analysis spot

The number of points to average was determined based on the values of the measurements in wet conditions. Standard error area corresponds to the standard deviation of a sample population. It will give the variation of the mean for all the possible draws of a sample out of a larger population. The SE area at 54 points will give the average variation for all the possible draws of 54 values out of 108. In the case of this thesis, the quality criterion chosen to determine the number of points is the SE of the 107th value. The SE area of this point is plotted in red in Figure 4.7. The impact of the last point is negligible compared to the weight of the 107 other values. Thus, the deviation is small.

After the average of 60 points, all the points remain in the SE area. Therefore, identical precision to the 108 measurements will be obtained with 60 points. After this experiment, it was decided to test concrete cubes in wet conditions and change the number of points from 108 to 60.



(a) Curve of the moisture impact on Fe_2O_3 (b) Curve of the moisture impact on CaO



(c) Curve of the moisture impact on SiO_2 (d) Curve of the moisture impact on Al_2O_3

Figure 4.7: Impact of the moisture on the weight percentage of Fe_2O_3 , CaO, SiO_2 , Al_2O_3 with the standard error area around the measurements done in wet condition.

4.1.5 Surface carbonation

The impact of surface carbonation on the content of CaO and SiO_2 was plotted in Figure 4.8. The appendix C.11 contains the remaining figures. The red curve represents the results obtained from concrete where surface carbonation occurred. The black curve presents the values obtained on a surface without surface carbonation. The value on the Y-axis corresponds to the weight percentage of the oxide (in %), and the value on the X-axis represents the number of measurements.



Figure 4.8: Impact of the carbonation on the weight percentage for SiO_2 and CaO.

In the first place, the amount of calcium detected at the surface increases due to surface carbonation. This outcome was expected due to the formation of calcium carbonate at the surface of the cube. The increase in calcium content results in an increase in the X-ray count rate generated by calcium elements. Weight percentage should decrease for the other elements based on the increase in the count rate for calcium atoms. This is the case only for SO_3 and SiO_2 . The other elements see their weight percentage increase in different proportions. This increase is probably due to the difference in the matrix between the two cubes. The surface tested on the carbonated cube would, in theory, have fewer aggregates than the surface of the noncarbonated cube. This theory is based on the idea that no increase should be detected for P_2O_5 , Al_2O_3 , TiO_2 and MnO. To validate this theory, Figures of appendix C.13 and C.2 were compared to the results in this section.

The curves obtained in the section C.2 show signs of local carbonation at point 5. The content of *CaO* and K_2O are significantly above the average, and the *SiO*₂ and *SO*₃ content are significantly below the average as for results in this section. Figures in appendix C.11 also show no impact of carbonation on P_2O_5 , Al_2O_3 , TiO_2 , and *MnO*.

If no significant change happens to these oxides due to carbonation, then another reason has to be found for their increase on the curves 4.8. The difference in the matrix between the two cubes would probably be the reason for this unexpected increase. Similar increases in MnO, TiO_2 , and Fe_2O_3 were noticed on a test led on a concrete cube containing fewer aggregates at the surface (Figures in Appendix C.13).

Finally, the increase in calcium content does not seem to affect the detection of manganese, iron, and titanium. These three elements have a higher atomic number. Therefore, the secondary X-rays emitted by these elements could enhance the detection of calcium by interacting with calcium electrons. However, none of the results lead to this conclusion. Therefore, no enhancement effect occurs with calcium.

4.1.6 Presence of aggregates at the surface

Measurements in section 4.1.1 showed a high concentration of SiO_2 (Figure 4.6a). Both CEM I 42.5N and aggregates contain SiO_2 in different proportions (see table 3.3). The content of cement does not exceed 20%. In the case of aggregates, it rises above 90%. Thus, the increase in weight percentage could originate from the analysis of aggregates at the surface. Furthermore, the difference in the weight percentage of SiO_2 for the results with the ESEM-EDS and hXRF could also prove the existence of aggregates at the surface. The analysis of SiO_2 with the ESEM-EDS gave a weight percentage of 24% when this percentage jumped to 28% for the hXRF. This difference in silica content can be explained by the difference in the area covered by the two beams. The area covered by ESEM-EDS is approximately equal to $11.3 mm^2$. This value equals 19.6 mm^2 in the case of hXRF. Therefore, a correlation can be established between the increase in silica content and the size of the area under analysis. These observations made it necessary to prove the presence of aggregates at the surface and determine their impact.



(a) Picture of the surface 1 with the digital microscope.



(b) Mapping of surface 1 with the ESEM-EDS.



(c) Picture of the surface 2 with the digital microscope.



(e) Picture of the surface 3 with the digital microscope.



(d) Mapping of the surface 2 with the ESEM-EDS.



(f) Mapping of the surface 3 with the ESEM-EDS.

Figure 4.9: Comparison of the mapping and picture for points 1, 2, and 3.

Pictures of the concrete surface and their corresponding silica mapping with the ESEM-EDS can be found in Figure 4.9. The pictures and the mappings in Figure 4.9 prove the existence of aggregates on the surface of the sample. These aggregates have different sizes, and only the big ones are visible in the pictures. The silica mappings also reveal the difference in aggregate size at the surface. Figure 4.9b shows the presence of aggregates with a size of fine sand in high quantities. Figure 4.9d also contains aggregates with fine sand size but in smaller quantities. Figure 4.9f shows only the presence of aggregates with the size of really fine sand.

When comparing the pictures with the silica mapping in Figure 4.9, aggregate particles can be recognized. The need to measure the $\frac{P}{A}$ ratio raised the question of paste covering the aggregates. The apparent surface (Figures 4.9a and 4.9c) might not reflect the surface analyzed by the X-ray beam. River gravels contain mainly silica oxide (see table 3.3). Therefore, mapping was done with the ESEM-EDS (Figures 4.9b and 4.9d) to obtain the content of SiO_2 through a similar depth to the X-ray beam. The shape of the coarser aggregates in Figures 4.9a and 4.9c does vary compared to their identification with mapping (see Figures 4.9b and 4.9d). The paste covers only the edges of the coarser aggregates in Figures 4.9a and 4.9c. Therefore, only the points on the paste surrounding coarser aggregates were counted as aggregates, not as paste.

Table 4.7: Table containing the average over 20 points of the P/A ratio and the area covered by paste and aggregates.

	Mean	SD
Area covered by paste(%)	75.58	4.56
Area covered by aggregates(%)	19.08	2.01
Paste over aggregate ratio (no unit)	4.02	0.63

Carbon marks done for the localization of ESEM-EDS measurements were present in the pictures. All points on these marks were discarded. After measuring the area covered by paste and aggregates, the results were averaged, as seen in the table above. This table shows that aggregates account for 20% of the total surface. The standard deviation is equal to 2% in the case of the surface covered by aggregates. This low value proves that the surface covered by aggregates does stay identical on most of the surfaces analyzed. It means that *CaO* and *SiO*₂ weight percentages vary moderately between measurements. The small variation of this ratio confirms the remarks in 4.1.1. It also proves that the position of the hXRF on the surface does not play a significant role.

Finally, the $\frac{P}{A}$ ratio is ten times higher compared to the expected $\frac{P}{A}$ ratio of the mix, which should be around 0.44. The wall effect can explain this difference in ratio. Fewer aggregates are present at the surface. Thus, the $\frac{P}{A}$ ratio increases.



Figure 4.10: Impact of matrix heterogeneity on measurements.

Based on the $\frac{P}{A}$ ratio and the respective chemical compositions of aggregates and cement, a theoretical model could be developed to predict the overall chemical composition of silica.

Concrete surfaces can be distinguished into three different types of surfaces as reproduced in Figure 4.10. The first corresponds to the surface occupied only by paste. Consequently, the equation states that the total SiO_2 content equals the value of SiO_2 in cement. The first degree of complexity comes with the presence of aggregates. The equation then changes, and aggregates are included in the equation as a factor that impacts the overall chemical composition. This equation can be found below the second drawing on the right. If this equation is used to predict the SiO₂ percentage, it reaches 32%. This value is off by 4% from the true value determined with the hXRF. Different factors can explain this difference in results. First, the distribution of aggregates is mostly homogeneous. However, reducing the surface area of the aggregates and paste to only one value will lead to errors. In addition, holes exist at the surface, as depicted in the last drawing. It is difficult to say what information will come out of a hole. Nevertheless, it might lead to the analysis of a deeper area since the X-rays move in a straight direction. The letter X in the equation represents this lack of information in Figure 4.10.

Do note that the results presented in the model reflect the measurements done on one CEM I 42.5N-based concrete cube.

4.2 Guideline and reproducibility

The experiments on concrete cubes were first performed with the hXRF before being conducted with the ESEM-EDS. These tests can be carried out separately. This thesis aims to provide a guideline on how to conduct hXRF tests. The guideline for the ESEM-EDS test is secondary in that it only provides a comparison with the hXRF results. Thus the guideline will be split into two parts.

4.2.1 Guideline

Guideline for the hXRF

	Guideline for hXRF
(-	Set-up for the experiment
۱ <u>-</u>	1 - Unwrap sample
ĺ.	2 - Place the cast surface on the left
C	3 - Draw the 6 lines
(4 - Warm-up the X-ray tube
0	5 - Verify the accuracy of the hXRF
C	6 - Wet the surface
(7 - Dry the surface
(Measurements
8 -	Measure the chemical composition on lateral surface l
(9 - Flip the cube on lateral surface Il
í.	10 - Draw the 6 lines
ĺ	11 - Wet the surface
	12 - Dry the surface
13	- Measure the chemical composition on

Figure 4.11: Guideline for the measurements done with the hXRF on CEM I-based concrete.

Unwrap sample: Cubes were wrapped to avoid surface carbonation during curing. Thus, the first task would be to remove the plastic foil.

Position the cast surface on the left: This step is necessary to ensure that the length of the cube from top to bottom is equal to 15 cm.

The 3D printed shapes are designed for a length of 15 cm (see Figure 3.10). A longer or shorter length would result in the wrong placement of these plastic pieces. Thus, flipping the cube is a way to ensure that the length is equal to 15 cm, as seen in Figure C.18. Another reason is the impossibility of measuring the chemical composition on the cast surface. The cast surface is uneven, and the concrete matrix at its surface differs from the lateral surface due to compaction.

Draw the 6 lines: The six lines are used to position the 3D printed piece. Plastic pieces should be placed with the left edge matching these lines. The lines should be placed at distances x_2 from the left edge of the cube (x_2 is equal to 20, 30, 45, 55, 70, and 80 mm). Special care should be taken to ensure the distance between the top and bottom of the cast surface is equal to 15 cm before drawing the lines. As explained in the previous step, the distance between the cast surface is not fixed. Thus, the distance x (see Figure C.18) might be higher or lower than 15 cm. When this is the case, the user of the hXRF should measure the difference between the distance x and the expected value of 15 cm. Then, the user should report it on x_2 .

Warm-up the X-ray tube: This action is needed for two reasons. The tube will emit more electrons at higher temperatures and gain in efficiency with the increase in temperature of the filament [70]. Therefore, one measurement was conducted on the concrete surface before the experiment. The measurement time was set to 300 seconds with a power of 15 kV in cement mode. This measurement was done in the middle of the cube for safety reasons.

Verify the accuracy of the hXRF: A standard sample is used to ensure that the calibration of the hXRF is accurate. The sample provided in this case had the chemical composition of a limestone sample. Thus, the mode to use was set to limestone. Its chemical composition was measured for 60 seconds at a power of 15 kV.

Wet the surface: This choice was made based on the results found in subsection 4.1.4. A dry cloth was soaked in water. Then, the surface was moistened with it. Water was left on the surface for 1 minute.

Dry the surface: Water could get through the plastic film protecting the detector and X-ray tube of the hXRF, and cause damage. Therefore, water on the surface was absorbed prior to measurements. The removal of water in excess was done with a clean and dry cloth.

Measure the chemical composition on the surface I: 36 measurements are done on surface 1 as shown in Figure 3.8. The measurements were done in a regular pattern and then randomized with the code depicted in Figure 3.18. The beam was shot for 30 seconds with a voltage of 15kV. Cement mode was used for these measurements.

Flip the cube on lateral surface II: The cast surface should be on the left. In this thesis, extra care was taken to compare the surfaces visually before measuring the chemical composition. This step is due to the unwanted surface carbonation of some parts of the cube caused by defectious wrapping, as explained in section 3.2.

Measure the chemical composition on surface II: 24 points were measured on the second surface. The measurements were done in a regular pattern and then randomized with the code depicted in Figure 3.18. The beam was shot for 30 seconds with a voltage of 15kV. Cement mode was used for these measurements

Guideline for the ESEM-EDS



Figure 4.12: Guideline for the measurements done with the ESEM-EDS.

Draw squares: Draw squares using the large 3D-printed shape first (see Figure 3.9). Then, use the smaller 3D piece to trace the squares used to recognize the area to analyze with ESEM-EDS (see Figure 3.9). All the lines should be traced with a carbon pencil. Carbon will not be analyzed with hXRF, and its detection can be disabled for ESEM-EDS analysis. The number of the surface should be marked on the top left corner (I or II), and the number of the sample should be written on the bottom right (1 to 9 for surface I and 1 to 6 for surface II).

Cut the samples: Cut the sample with a blade. The blade thickness should not exceed 4mm to avoid damaging the area that will be analyzed with the ESEM-EDS. Dry cut if possible. The absence of water will limit the formation of calcium carbonate crystals at the surface and, at the same time, decrease the difference in the chemical composition of the surface between the measurements with the hXRF and the ESEM-EDS.

Store the samples: Store the samples in a climate chamber with 0% RH and a temperature of 60°C.

Measure the chemical composition with the ESEM-EDS: 60 points were analyzed using the ESEM-EDS. Squares represented these points on 15 samples (see Figure C.7). Their chemical composition was acquired using an electron beam with an energy of 15 keV and a magnification of 100×. The beam was shot for 90 seconds. The detection of calcium, silicon, aluminum, iron, magnesium, potassium, phosphorus, sulfur, titanium, and manganese was forced. The detection of sodium and carbon elements was disabled.

The whole guideline for this thesis can be found in the appendix C.19

4.2.2 Reproducibility

Reproducibility is defined as the possibility for scientists to obtain the same data and analysis from previous scientific findings by reproducing the experiments [71]. The definition is vague, and there is no general classification to determine if the results are reproducible. Thus, reproducibility is assessed differently for each scientific research. This study defines reproducibility as the capacity to identify CEM I-based concrete cubes with identical composition.

Initially, the curves of the CEM I-based cubes were plotted with their respective standard error (SE) area in Figure 4.13. The curves for all the different oxides can be found in appendix C.20. This first step was done to see if the results were overlapping. Ideally, every CEM I cube with the same design should give identical results.



Figure 4.13: Test of the reproducibility with two cubes of CEM I-based concrete for *CaO* and *SiO*₂.

First, no curves overlap in Figure 4.13. Sets of measurements on two cubes with the same conditions yield different results. In theory, the only difference between the two experiments is the concrete matrix. Thus, from these results, it can be concluded that the matrix affects the measurements. It means that the concrete surface changes from cube to cube.

The three elements present at the surface are aggregates, pores, and paste. Thus, if the results change as they did here, it means that the number of elements analyzed on the two cubes differed. The weight percentage in SiO_2 is high for the second cube (blue curve). The cubes were cured in perfect condition (perfect sealing in a dry environment) in contrast to the previous cube. Therefore, they were not wet after being unwrapped. As a result, the water poured on top for a minute was absorbed faster. It explains the higher SiO_2 content for both cubes in Figure 4.13b compared to the previous cubes (see Figure 4.6a). In addition, both cubes have a silica oxide content close to or higher than the SiO_2 content for the test done on the dry cube in section 4.1.4. This observation supports the assumption that the two cubes were fully dried after curing.

The difference in SiO_2 content between the two cubes might be explained by two possible factors: a higher porosity, in which the water might get soaked in faster, or a higher amount of aggregates on the surface. It is probably a combination of those two effects. The weight percentage of the light elements Al, Si, and P is higher for the cube CEM I 2. A lower moisture content increases the weight percentage of lighter elements, as observed in section 4.1.4. The matrix of the two cubes was probably also affected by the little volume cast. Only 15L was cast for this experiment. The matrix varies more in the case of small volumes.



Weight percentage of the oxide Al2O3 5.8 CEM I 1 56 CEMI 2 weight percentage (%) 10%FA 5.4 10%slag 5.2 5.0 4.8 4.6 4.4 4.2 40 60 10 20 30 50 number of measurements

Comparison between the two CEM I cubes and the cubes containing 10% GGBFS and 10%FA for *CaO*

Comparison between the two CEM I cubes and the cubes containing 10% GGBFS and 10%FA for Al_2O_3

Figure 4.14: Comparison between the two CEM I cubes and the cubes containing 10% GGBFS and 10% FA for CaO and Al_2O_3 .

If results are not reproducible, they might be compared to the mixes with the closest chemical composition, as seen in Figure 4.14. The other Figures are in appendix C.21. The possibility to create a threshold for each mix in which all results obtained from this mix would fall within. The two results obtained on different CEM I cubes were plotted with results for 10% GGBFS and 10% FA. In theory, adding SCMs should lead to a decrease in *CaO* content. This decrease in *CaO* should be stronger in the case of 10% FA.

Adding SCMs would also increase SiO_2 content. This increase should be higher in the case of 10% FA than in the case of 10% GGBFS. The Al_2O_3 content should increase with a similar tendency as SiO_2 . In the case of Fe_2O_3 , the trend of 10% FA and 10% GGBFS should be opposite. The iron content in FA is lower than in PC, which is higher in GGBFS than in PC. Thus, 10% FA should have a lower content of Fe_2O_3 while 10% GGBFS should have a higher content than CEM Ibased concrete. These interpretations were based on the table 3.3.

However, most of the curves for those elements overlap. This overlap is mainly due to the high content in SiO_2 of the cube CEM I 2. The curves for SiO_2 , Fe_2O_3 and CaO content overlap. These elements cannot be used to differentiate the mixes due to the overlap of the curves. Some oxides show interesting curves as for TiO_2 , SO_3 , Al_2O_3 and K_2O . These curves follow the expected order, and none of the curves overlap. Those elements could theoretically be used to differentiate CEM I with 10% FA and 10% GGBFS.

Ratios between the oxides that gave significant results were calculated and presented in the table 4.8. The optimal ratio would be a ratio that could help differentiate mixes while giving a similar result for CEM I.

Ratio	CEM I 1	CEM I 2	10% FA	10% GGBFS
$\frac{TiO_2}{SO_3}$	0.144	0.140	0.267	0.257
$\frac{TiO_2}{Al_2O_3}$	0.110	0.0980	0.0955	0.115
$\frac{TiO_2}{K_2O}$	0.681	0.777	0.608	1.05
$\frac{Al_2O_3}{SO_3}$	1.32	1.43	2.79	2.23
$\frac{Al_2O_3}{K_2O}$	6.22	7.92	6.37	9.13
$\frac{SO_3}{K_2O}$	4.72	5.54	2.28	4.09

Table 4.8: Ratio between Al_2O_3 , SO_3 , K_2O , TiO_2 .

Most ratios offer limited results, as seen in Table 4.8. Some ratios, such as the ratio between TiO_2 and SO_3 , show a difference in the ratio between CEM I and the other mixes. However, the difference between 10% GGBFS and 10%FA is too small to differentiate the two mixes. The inverse is also true in the case of SO_3 and K_2O . For this ratio, the difference between 10% FA and 10% GGBFS is significant enough to be compared, but the difference between the two results for CEM I is too large compared to the two other mixes. The interesting ratio to compare CEMI to 10% FA and 10% GGBFS is the ratio between Al_2O_3 and SO_3 .

4.3 Impact of the grading of the aggregates

The maximum size of aggregates changed through the twentieth century, as explained in Table 2.2. The Dutch standards stipulate that aggregate size should not exceed 31.5 mm. This thesis tested three different gradations: 0-8 mm, 0-16 mm, and 0-32 mm. The most relevant element to look at in the case of aggregates is the weight percentage of SiO_2 . This quantity was expressed as a function of the number of points for the three different mixes in Figure 4.15. The respective SE areas were added to the curves. The other Figures are in appendix C.22.



Figure 4.15: Impact of the grading of the aggregates on the SiO_2 content.

Figure 4.15 shows that the SiO_2 content for the three different mixes is close. The silica content overlaps for 0-16 mm and 0-32 mm. In the case of 0-8 mm, the SiO_2 content is lower. This finding is counterintuitive. The mould imposes a packing of aggregates at the surface. This packing of aggregates inside the concrete leads to an accumulation of small aggregates (less than 1 mm in diameter) at the surface. The mix 0-8 mm contains approximately 41% of particles with a diameter of less than 1 mm. This number decreases in the case of 0-16 mm, reaching 33%, and drops to 17% for 0-32mm mixes (see table B.3). In theory, the increase in small particles would lead to a higher aggregate density at the surface.

However, the density drops with the decrease in the gradation of the aggregates. Cohesive forces exerted by particles on one another drive the packing of smaller particles. These forces still exist for larger aggregates but are neglected due to gravitation and shear forces. Cohesive forces result in dense clusters of particles separated by highly porous areas. This layout will, in the end, result in a lower density packing and fewer aggregates at the surface [65]. Thus, the 0-8mm mix has a lower density of aggregates at the surface. Furthermore, the packing density of a mix will increase with a larger particle distribution. Smaller particles fill the voids between the larger particles.

The chemical composition of the rest of the elements increases proportionally to the decrease of SiO_2 content. The number of counts detected from silicon is lower, giving more weight to the rest of the elements.

4.4 Overview of the chemical composition for concrete blended mixtures

The overall mixes with different cementitious materials in different ratios were plotted in Figure 4.16. In addition, their respective SE area was plotted to see if the same weight percentage between various mixes could be obtained. The other Figures are in appendix C.24. Those curves summarize what has already been seen in prior studies regarding reproducibility and the many factors impacting the results.



Weight percentage of the oxide Al2O3 12 10% slag 20% slag weight percentage (%) 30% slag 10 40% slag 50% slag 60% slag 8 70% slag 80% slag 10% FA 6 20% FA 30% FA 40% FA 4 CEM I 10 20 зό 40 50 60 number of measurements

Weight percentage of $Fe_{2O}3$ for all the mixes designed in this thesis



Figure 4.16: Weight percentage of Fe_2O_3 and Al_2O_3 for all the mixes designed in this thesis.

First, the wrapping did not work on all the cubes, and some had carbonated surfaces. The effects can be seen for 20% GGBFS compared to 30% GGBFS. The *CaO* content in GGBFS is lower than in CEM I 42.5N cement. Therefore, a higher content of GGBFS should result in a lower weight percentage of calcium oxide. However, the weight percentage of *CaO* for 30% GGBFS is higher than that of 20% GGBFS. A hypothesis could be that SiO_2 content impacts the results due to a higher density of aggregates at the surface for 20% GGBFS. The K_2O content of 20% is lower. The K_2O content in GGBFS is higher than in Portland cement. Thus, the value for K_2O in the case of 30% GGBFS should be lower than the one for 20% GGBFS. This result proves that calcium carbonate formed on the surface of the cube containing 30% GGBFS.

The increase in CaO will lead to a reduction of the signal for SiO_2 causing a decrease in SiO_2 weight percentage as explained in section 4.1.5. This decrease is also observed in the case of 30% GGBFS.

In the case of 40% GGBFS, the main issue seems to be the higher density of aggregates at the surface compared to 50% and 60% GGBFS. The amount of SiO_2 is higher by 5% for 40% GGBFS causing the drop in content of the other elements as experienced in the section on reproducibility (see section 4.2.2).

The curves of SO_3 , K_2O cannot be compared due to their too-high overlap. The curves overlap due to a high SE area and a low variation in the averaged composition from mix to mix. In the case of these elements, the cementitious materials have a low variation in their weight percentages.

 SiO_2 cannot be used to distinguish the mixes because it changes too much according to the aggregate density at the surface. *CaO* is an oxide highly sensitive to surface carbonation. Therefore, assessing the possibility of separating mixes using this oxide is difficult. Finally, the only oxide giving interesting results is Al_2O_3 and Fe_2O_3 . However, Fe_2O_3 seems to be sensitive to carbonation effect based on the observations for 20% and 30% GGBFS. The position of 20% GGBFS should be above and not below 30% GGBFS. Differentiating 12 out of the 14 mixes according to Al_2O_3 oxide is possible. Only 40% FA and 50% GGBFS overlap for this element, and the other SE areas are distinct after 28 measurements. Furthermore, the number of points needed for differentiating the mixes could be optimized and changed from 60 to 28 points

Chapter 5 **Discussion**

The definition of lightweight elements in the literature review is vague as it depends on the technique and sample matrix. Lightweight elements are more affected by the calibration and factors affecting the results. Therefore different definitions exist in the literature review. The definition of lightweight elements regroups elements between magnesium and phosphorus in the case of plant analysis [72]. However, this definition is extended to elements up to potassium in studies done on petrographic samples [66]. The matrix and elements detected in concrete are closer to the matrix of rocks. Thus, the expectation would be to see all the elements with an atomic number below calcium being defined as lightweight elements. The experiment in section 4.1.4 confirms this hypothesis. In this experiment, all the elements are affected by moisture. However, two different behaviors emerge from the impact of water. Water attenuates the weight percentage of elements with an atomic number below 20, while the weight percentage of the elements with an atomic number above or equal to 20 increases. The reason behind this is the higher impact of moisture on elements with an atomic number below 20. Moisture impacts less the other elements. Their weight percentage increases due to the normalization of the results to 100%. Therefore, the lightweights elements in concrete appears to be all the elements with atomic number below 20.

hXRF in theory does detect elements from magnesium up to uranium. However, magnesium was only detected occasionally for mixes with a GGBFS content above 70%. Yundakul et al., in their research on the analysis of fresh concrete with an hXRF did not detect the presence of magnesium in the paste(see [63]).

The impossibility to detect magnesium might be due to three different reasons. Magnesium distribution might not be homogeneous over the surface, or this element is absent. A too high amount of X-rays are absorbed by moisture, matrix or air. The detection of magnesium is not possible with the calibration used by Bruker. The mapping of the presence of magnesium at the surface contradicts the first argument. This mapping is depicted in figure 5.1.



Figure 5.1: Mapping of the magnesium at the surface.

This mapping shows various points at the surface corresponding to magnesiumrich phase. These mineral phases are randomly and homogeneously spread at the surface. Their size do not exceed 50 μm as most hydration of the periclase phase contained in cement is difficult at ambient temperature. Only smaller phases will hydrate, and the larger ones will hydrate partially. Therefore, their presence in large quantities and homogeneously spread all over the surface contradicts the first argument.

The absorption of secondary X-rays by moisture and air is unavoidable. The air between the rough concrete surface and the detector absorbs some of the secondary X-rays coming from the sample. The absorption of X-rays by moisture is due to capillary water, adsorbed water, and interlayer water in concrete. The experiment in section 4.1.4 proves the absorption of secondary X-rays by capillary water. Furthermore, these results determined that lighter elements would be more generally affected. However, the impact of the moisture is not proportional to the atomic number. The article [63] also raised this concern after integrating the impact of water in their mathematical model predicting the amount of SCM. The accuracy of the model dropped with the addition of water in the model.

Finally, the impossibility of detecting magnesium might be due to the calibration limit used by the hXRF. The limit of detection is proportional to the standard deviation. The standard deviation of magnesium is the highest as this element is the lightest element detectable by the hXRF. Therefore, its precision will be the lowest. The LOD of the Niton XL3t900GOLDD for a silica oxide matrix is around 3500 ppm, and the LOD of the Bruker S1 Titan 800 in a cement mode is equal to 3000 ppm. These two values are close considering the gap between them and the LOD for aluminum, respectively equal to 500ppm and 450ppm. The detection limit for aluminum is approximately seven times lower than the LOD of magnesium in both cases. The percentage error of alumina in section 4.1.4 equals 20%. This result proves that capillary moisture causes a drop of 20% in the detection of alumina. This number is even higher when comparing powder to paste based on the data from the article [63]. These data are interesting as the Niton XL3t900 does not normalize the weight percentage of the oxides to 100%. The value labeled 'balance' regroups all the x-rays detected but not assigned. Therefore, these results depict the matrix's impact on the detection of elements. The percentage error between the results obtained for the Portland cement powder and paste were calculated and are shown in table 5.1.

Oxide	Percentage error (%)		
CaO	23.03		
SiO ₂	19.38		
Al_2O_3	36.78		
Fe_2O_3	28.94		
MgO	100		
K_2O	20.78		
SO ₃	18.60		
TiO ₂	25		
Mn_2O_3	31.25		

Table 5.1: Percentage error of the different oxides for ordinary Portland cement. Based on results from the research led by Yundakul et al. [63].

The percentage errors obtained in table 5.1 are higher than the error caused by the presence of capillary water. The error for alumina content between the measurements done on paste and powder rises up to 37%. It almost doubles compared to the error caused by capillary moisture. The paste was tested one day after curing in the research led by Yundakul [63]. The fresh paste contains some capillary water, interlayer, and adsorbed water. Therefore, the comparison between fresh paste and powder provides a higher source of error than the comparison of dry and wet concrete. Consequently, the LOD of the hXRF seems too high to detect the presence of magnesium in concrete.

Overall, the impossibility of detecting magnesium resides in a less suitable calibration and the attenuation of the X-rays due to the presence of air and moisture.

The cement mode was configured with the analysis of powders as explained in 3.4. The consistent source of error caused by the concrete matrix and the presence of moisture raises questions about whether cement mode from the Bruker S1 Titan 800 can be used to test concrete. Yundakul et al. compared the data from the Portland cement powder measured with the hXRF to the international norm ASTMC150. The comparison showed that all the results except for SO_3 conform to this norm. The percentage error in table 5.1 between the measurements done on Portland cement powder and paste revealed the complexity of measuring the paste composition. The consistent error originating from the matrix and water interference raises the concern that a calibration done on powder will not be appropriate for measurements done on solid samples.

The higher impact of factors on lightweight elements raises the question of the elements to differentiate the mixes. The results in this thesis proved that mixes could be differentiated based on comparing their alumina content. Nevertheless, the results in the section 4.2.2 prove that cubes with identical mix designs will provide different results. Therefore, nothing can be said about the reproducibility of the results from other cubes. The first option might be to measure the chemical composition of many cubes to obtain a point cloud and determine the threshold values for each oxide. However, the difference of average for oxide showing no overlap is already close (10 mixes out of 13 have an alumina content between 6 and 11%). Therefore, the threshold of all the mixes will overlap. A possible solution to remedy this issue would be to compare a certain number of oxides together instead of trying to differentiate the mixes based on the weight percentage of a single oxide. The Bruker S1 Titan 800 offers the possibility to create new calibrations by entering the expected values of each oxide. The threshold values could be set as calibration for each mix. Then, the hXRF would determine the mix based on the results of all the oxides. Nevertheless, all the elements might not give the same quality of results. Precision is proportional to concentration and atomic number, as proved in section 4.1.2. The precision for most elements in higher concentration is identical for hXRF and ESEM-EDS (RSD is below 10%). The choice of the elements can be extended to the elements showing good precision between the hXRF and ESEM-EDS measurements. Therefore, the weight percentage of calcium oxide, silica, alumina, iron oxide, titanium oxide, and potassium oxide can be compared to determine the concrete mix. Phosphorus oxide, manganese oxide, and sulfur oxide should not be compared as their precision is low compared to the ESEM-EDS. An unknown resides in the fact that the study on precision was done on CEMI-based concrete cubes. The precision associated to P_2O_5 , SO_3 , MnO might increase if their concentration increases. Similarly, the precision of the elements with a good correlation might decrease if their concentration decreases.

The surface of the concrete is a highly heterogeneous, multi-scale, multiphasic material. Therefore, a single measurement might not give accurate and precise results to differentiate concrete. A few measurements should be averaged in order to obtain reproducible results and increased accuracy. No previous study led on concrete stated the optimal number of measurements to average. The moving average calculated for 2 to 108 measurements might provide insight on the optimal number for identification of the mixes.

First, the number of points was set to 108. Then, this number was reduced to 60 with the use of the standard error (SE) of the 107th point (see section 4.1.4). Finally, this number was lowered to 28 after the comparison of the alumina content in all the mixes. These values are high compared to the existing data. The decision made on the number of measurements was based on highly selective criteria. No previous study was led on the impact of factors on measurements of concrete with an hXRF. Therefore, the decision was made to set the criteria highly selective to ensure that the precision of the results would be high and experiments would be reproducible.

The research led by Bourke et al. [73] on petrographic samples calculated the gain in precision with a moving average from 3 up to 29 measurements. Results revealed that the main gain in precision is obtained with an average of 3 to 7 measurements for the most abundant elements. The same article specifies that 17 measurements need to be averaged to obtain an RSD below 10% for all the elements. Rocks used in this article can be assumed to be more homogeneous than concrete as the RSD for all the elements went below 10% with an average of 17 or more measurements. In the case of concrete, most of the elements will have an RSD below 20% with an average of 7 measurements. An RSD of 20% or below means, accordingly to the U.S. EPA criteria, that the correlation between the two techniques is good. Nevertheless, taking only seven measurements might be risky as the fluctuation of the RSD decreases with the number of points. Based on this last observation and the curves in the section C.11, the optimal number of points to average seems to be equal to 20.
Chapter 6

Conclusion and Recommendation

6.1 Conclusion

The objective of this master's thesis was to provide knowledge on non-destructive testing of cement and supplementary cementitious materials composition in concrete with a handheld-XRF. This objective was fulfilled by analyzing concrete cubes with different compositions. The mixes reflect the concrete design used in the Netherlands for concrete infrastructure. Experimental programs conducted on concrete revealed the impact of different factors. These factors are the measurement time, moisture, surface carbonation, and matrix effect. Each factor impacts various oxides in different proportions. Therefore, each of these factors depicts a distinct pattern.

Among these factors, moisture, surface carbonation, and matrix effect have the highest impact. Moisture does impact all the elements. However, all the elements with an atomic number below 20 are more attenuated than the rest. The other elements see their weight percentage increase due to the normalization of the weight percentage to 100%. In the case of surface carbonation, experiments proved that the weight percentage of CaO, Fe_2O_3 and K_2O oxide increases while the weight percentage of SiO_2 and SO_3 decreases. Surface carbonation does not impact the rest of the elements. The formation of calcium carbonate crystals at the surface justifies the increase of calcium oxide. The covering of the aggregates by calcium carbonate crystals explains the decrease in the detection of silica at the surface. The impact of the matrix is due to the composition of the paste, the presence of aggregates at the surface, and the pore system. This thesis highlights the presence of aggregates at the surface. Their presence on the surface increases the silica content detected by the hXRF. Silica concentration is expected to vary highly due to the presence of aggregates on the surface. Even if the precision for silica is lower than the rest of the main elements, its concentration detected with the hXRF did stay stable. Research done in this thesis shows that aggregate density for a gradation of 0/16 mm stays homogeneous at the scale of hXRF measurements. Nevertheless, this might not be the case for all gradations. A lower silica content was detected for the lowest gradation used in this thesis (0/8mm). This lower silica content is counterintuitive as a larger fraction of smaller aggregates would, in theory, increase the aggregate density at the wall of the concrete cube. Nevertheless, smaller aggregates will lead to a higher heterogeneity of the aggregate density at the surface as the cohesive forces drive the packing of smaller particles.

The impact of the pores was discovered in the study led on the reproducibility of the guideline. The porosity of one of the cubes was higher, leading to faster water absorption at its surface. This last point raises the question of the validity of the guideline created in this thesis. This guideline is the first ever written to test concrete with an hXRF. As this thesis aimed to limit the factors impacting the hXRF measurements and test all the mixes in reproducible conditions, it was decided to compare the results with ESEM-EDS measurements. Nevertheless, the decision to test samples in moist conditions based on ESEM-EDS results is questionable. This choice does not take into account the morphology of concrete. Concrete porosity is responsible for the permeability of concrete. The volume of pores changes for each cube. Thus, wetting the surface will result in an uncontrolled moisture content on the concrete surface. Therefore, it would be preferable to dry the cube rather than wet it. The other choices made in the guideline did not represent an issue with the reproducibility of the experiments. Furthermore, the difference in weight percentage found in this experiment showed that oxide concentration for each mix is not represented by a single value but thresholds. This notion of threshold raises the question of overlap between the different chemical compositions of the mixes. Thus, the solution to this issue is to set a threshold for each oxide of each mix. The comparison of multiple oxides to determine the mixes is necessary in that case.

Nevertheless, the weight percentage of Al_2O_3 appears in this thesis to be not impacted by concrete matrix and surface carbonation. This element proved that mixes could be differentiated even if surface carbonation and moisture content differences did occur at the surface. These two factors could not be controlled in the test led on all the mixes as the plastic film used to wrap the samples did fail. This oxide allows the differentiation of all the mixes except those containing 50% GGBFs and 40% FA in less than 28 points. Considering that the mixes should be identified by comparing multiple elements, the choice of the elements to identify the mixes was debated in the discussion. The choice was made depending on the elements showing a good correlation with the ESEM-EDS measurements. All the oxides contained in concrete could be used to identify the mix design except P_2O_5 , SO_3 , and MnO. These oxides have low precision. Low precision implies that results highly vary from measurement to measurement. The number of measurements was reduced to 20 based on the RSD of the elements selected to identify the mixes. The number of points and the choice of oxides to consider for the differentiation of the mixes were decided based on results obtained in wet conditions.

Another critical point is the position of the measurements on the concrete surface. The measurement pattern does not impact the accuracy of the results. Therefore, measurements should be taken in a random pattern to gain time. The measurement time should also be set to 30 seconds to gain time. A higher measurement time will not increase the accuracy or the precision.

6.2 Recommendation

This study is innovative in the scientific domain due to the few types of research done on concrete with an hXRF and the deep study of the impact of factors. Few materials as complex as concrete were tested with the hXRF. Concrete by its matrix complexity but also its chemical composition has a lot to offer for the understanding and improvement of the use of X-rays on-field. Therefore, recommendation will be provided for future studies on the subject.

One of the biggest issues of this project is the adaptation of the detection of concrete from the controlled environment in the laboratory to the outside world. Based on the existing knowledge, the difference in the two environments lies in the presence of moisture and carbonation of concrete. These two factors were tested in an uncontrolled way in this thesis due to the failure of the plastic wrapping in the curing room. This failure benefits the further researches as it proves that moisture and surface carbonation can be identified with the hXRF. This error proved that these two factors does impact less the weight percentage of alumina. The differentiation of mixes with alumina was possible even with the proof that some samples suffered from surface carbonation or water absorption of the X-rays. This element might, therefore, be central in the identification of concrete in-situ. The impact of surface carbonation and variation in moisture content should be studied further in detail. The impact of the variation of moisture content could be studied using a climate chamber. The impact of the moisture content should be studied on a single cube as the matrix impacts the results. Carbonation of the sample could be reproduced by placing cubes in a carbonation box.

Another option would be to limit these two parameters on-site. The concrete surface could be dry with an hot air gun prior to measurements. The determination of the optimal drying time with the hot air gun could be calculated by comparing the results with measurements done on a dry cube. The sample tested should also have a low calcium content to limit the carbonation caused by the cyclic wetting of the sample. The removal of calcium carbonate from the surface is more complicated as the carbonation rate depends from the environment, time of exposure and concrete mix design. However, the removal of surface of carbonation in early carbonation might be possible by scrubbing the surface. However, this action would expose more aggregates. The higher area covered by aggregates would then affect the hXRF measurements.

The difference of aggregate density and porosity at the surface appeared to be another limiting factor in the possibility to determine the mixes based on their chemical composition. One option offered in this thesis was to test many samples to determine the chemical composition thresholds for each mix. Another study should be led on the impact of the sample geometry prior to this test which requires the casting of many samples and is time consuming. Smaller volumes of concrete present a higher source of heterogeneity due to the higher source of error during their casting. Therefore, a higher volume of concrete tested with the updated version of the guideline would possibly lead to reproducible results.

Appendix

Appendix A

A.1 Formula

Bragg's law:

$$n \cdot \lambda = 2 \cdot d_{hkl} \cdot sin(\theta) \tag{A.1}$$

n: order of diffraction

 λ : X-rays wavelength

 d_{hkl} : interplanar spacing

 θ : incident and diffraction angle

A.2 Definition

- *high total dissolved solids (TDS)*: Measure of the dissolved combined content of all inorganic and organic substances present in a liquid.
- *Quantitative measurements*: accurate measurement of the elemental concentration.
- *Semi-quantitative measurement*: Estimation of the elemental concentration.
- *Qualitative measurements*: detection or identification of the components inside concrete.
- Primary X-rays: X-rays sent via the hXRF.
- *Secondary X-rays*: X-rays coming out of the sample. They result from the de-excitation of the electrons inside the sample.

Appendix B

Tables

Table B.1: Cement chemists' notation

Oxide	<i>Ca</i> 0	SiO ₂	Al_2O_3	Fe_2O_3	H_2O	Na_2O	<i>K</i> ₂ 0	SO_3	MgO	CO_2
Symbol	С	S	А	F	Н	N	K	\overline{S}	М	\overline{C}

Table B.2: Mineralogical information given by techniques on concrete

Technique	Chemical composition	Mineralogical composition
PLM		Х
SEM-EDS	Х	Х
ICP	Х	
Desktop-XRF	Х	
LIBS	Х	
hXRF	Х	

sieve opening (mm)	0-8mm (%)	0-16mm (%)	0-32mm (%)
0.125	0.37	0.46	0.34
0.25	4.21	3.64	3.01
0.5	24.66	20.00	16.99
1	40.81	32.89	28.05
2	47.72	38.55	32.79
4	53.52	44.51	36.94
8	96.44	64.98	47.14
16	100	99.44	55.39
31.5	100	100	100

Table B.3: Table of the sieving of aggregates with the norm NEN-EN 12620 in percent

|--|

Compound	density $(kg \cdot m^{-3})$
CEM I 42.5N cement	3150
GGBFS	2900
FA	2440
Aggregates	2650
water	1000

Table B.5: Composition of the 16 mixes

compound	mix 1	mix 2	mix 3	mix 4	mix 5	mix 6	mix 7
Water (kg)	13.0	2.9	2.9	2.9	2.9	2.9	2.9
cement (kg)	25.9	5.1	4.6	4.0	3.4	2.9	2.3
slag (kg)	0.0	0.6	1.00	1.6	2.1	2.6	3.1
fly ashes (kg)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Fine Aggregates (kg)	58.4	12.4	12.4	12.4	12.4	12.4	12.4
Coarse Aggregates (kg)	69.2	14.6	14.6	14.6	14.6	14.6	14.6
Total volume (L)	70	15	15	15	15	15	15

Composition of the 16 mixes

		-					
compound	mix 8	mix 9	mix 10	mix 11	mix 12	mix 13	mix 14
Water (kg)	2.9	2.9	2.9	2.9	2.9	2.9	2.9
cement (kg)	1.7	1.1	0.6	5.1	4.6	4.00	3.4
slag (kg)	3.7	4.2	4.7	0	0	0	0
fly ashes (kg)	0	0	0	0.4	0.9	1.3	1.8
Fine Aggregates (kg)	12.4	12.4	12.4	12.4	12.4	12.4	12.4
Coarse Aggregates (kg)	14.6	14.6	14.6	14.6	14.6	14.6	14.6
Total volume (L)	15	15	15	15	15	15	15

Composition of the 16 mixes

compound	mix 15	mix 16
Water (kg)	5	4.5
cement (kg)	10	9
slag (kg)	0.0	0.0
fly ashes (kg)	0.0	0.0
Fine Aggregates (kg)	25.5	18.4
Coarse Aggregates (kg)	18.5	27.7
Total volume (L)	25	25

Table B.6: Repartition of each element present at the surface in percent

Element	point1	point2	point3	point4	point5	point6	point7	point8
Paste	70.40	76.53	67.54	68.23	70.77	65.45	75.76	77.00
Aggregate	22.87	19.39	18.32	19.27	22.56	21.47	20.20	18.50
Voids	6.30	4.08	14.14	12.50	6.67	13.09	4.04	4.50

Repartition of each element present at the surface in percent

point9	point10	point11	point12	point13	point14	point15	point16
77.00	78.50	82.00	77.00	78.50	79.50	77.00	76.50
18.50	20.00	17.50	20.00	16.50	18.00	20.00	17.50
4.00	3.00	5.50	1.50	1.50	5.00	1.50	3.00

Repartition of each element in percent

point17	point18	point19	point20
80.00	79.50	77.50	77.00
19.50	18.50	14.00	19.00
3.50	5.00	6.00	1.50

Appendix C

Curve plots and graphics

C.1 Method



(a) Sieve analysis grading curve for 0/8mm aggregates



(c) Sieve analysis grading curve for 0/32mm aggregates

Figure C.1: Sieve analysis grading curve for different fractions. Reproduced from [74].



(a) Sealing done on 16 mixes

(b) Sealing done on copper samples

(c) Sealing done on mixes to test reproducibility

Figure C.2: Pictures of the different types of sealing done for concrete samples



Figure C.3: Cutting pattern for the three concrete cube surfaces.



Figure C.4: Picture of the shape used to draw the lines for the cutting of the smaller samples.



Figure C.5: Drawing of the points and square delimitation on the concrete surface.



Figure C.6: Picture of the six moulds created to position the hXRF.



Figure C.7: Picture of the aluminum tray containing the samples.

C.2 Impact of the sample edges



Evolution of the *CaO* content through the length of the concrete surface.



Evolution of the Al_2O_3 content through the length of the concrete surface.



Evolution of the *MgO* content through the length of the concrete surface.



Evolution of the SiO_2 content through the length of the concrete surface.



Evolution of the Fe_2O_3 content through the length of the concrete surface.



Evolution of the SO_3 content through the length of the concrete surface.



Evolution of the P_2O_5 content through the length of the concrete surface.



Evolution of the K_2O content through the length of the concrete surface.



Evolution of the TiO_2 content through the length of the concrete surface.



Evolution of the MnO content through the length of the concrete surface.

Figure C.8: Evolution of the oxides content through the length of the concrete surface.

C.3 Impact of the sample edges (bell curves)



Bell curves of the *CaO* content through the length of the concrete surface.



Bell curves of the Al_2O_3 content through the length of the concrete surface.



Bell curves of the *MgO* content through the length of the concrete surface.



Bell curves of the SiO_2 content through the length of the concrete surface.



Bell curves of the Fe_2O_3 content through the length of the concrete surface.



Bell curves of the SO_3 content through the length of the concrete surface.



Bell curves of the P_2O_5 content through the length of the concrete surface.



Bell curves of the TiO_2 content through the length of the concrete surface.



Bell curves of the MnO content through the length of the concrete surface.



Bell curves of the K_2O content through the length of the concrete surface.



Bell curves of the TiO_2 content through the length of the concrete surface.



Bell curves of the MnO content through the length of the concrete surface.

Figure C.9: Bell curves of the oxides content through the length of the concrete surface.

C.4 Measurement time of 10, 20, 30 seconds



Evolution of *CaO* content versus the number of points for 10, 20, 30 seconds



Evolution of Al_2O_3 content versus the number of points for 10, 20, 30 seconds



Evolution of *MgO* content versus the number of points for 10, 20, 30 seconds



Evolution of SiO_2 content versus the number of points for 10, 20, 30 seconds



Evolution of Fe_2O_3 content versus the number of points for 10, 20, 30 seconds



Evolution of SO_3 content versus the number of points for 10, 20, 30 seconds



Evolution of P_2O_5 content versus the number of points for 10, 20, 30 seconds



Evolution of K_2O content versus the number of points for 10, 20, 30 seconds



Evolution of TiO_2 content versus the number of points for 10, 20, 30 seconds



Evolution of *MnO* content versus the number of points for 10, 20, 30 seconds

Figure C.10: Evolution of the oxides content versus the number of points for 10, 20, 30 seconds.

C.5 RSD for measurement time of 10, 20, 30 seconds



Evolution of the relative standard deviation for *CaO* versus the number of points for 10, 20, 30 seconds



Evolution of the RSD for Al_2O_3 versus the number of points for 10, 20, 30 seconds



Evolution of the RSD for *MgO* versus the number of points for 10, 20, 30 seconds



Evolution of the relative standard deviation for SiO_2 versus the number of points for 10, 20, 30 seconds



Evolution of the RSD for Fe_2O_3 versus the number of points for 10, 20, 30 seconds



Evolution of the RSD for SO_3 versus the number of points for 10, 20, 30 seconds



Evolution of the RSD for P_2O_5 versus the number of points for 10, 20, 30 seconds



Evolution of the RSD for K_2O versus the number of points for 10, 20, 30 seconds



Evolution of the RSD for TiO_2 versus the number of points for 10, 20, 30 seconds



Evolution of the RSD for *MnO* versus the number of points for 10, 20, 30 seconds

Figure C.11: Evolution of the RSD for the oxides versus the number of points for 10, 20, 30 seconds.

C.6 Measurement time of 30, 60 seconds



Evolution of the CaO content versus the Evolution of the SiO_2 content versus the number of points for 30, 60 seconds number of points for 30, 60 seconds



Evolution of the Al_2O_3 content versus the Evolution of the Fe_2O_3 content versus the number of points for 30, 60 seconds number of points for 30, 60 seconds



Evolution of the MgO content versus the Evolution of the SO_3 content versus the number of points for 30, 60 seconds number of points for 30, 60 seconds



Evolution of the P_2O_5 content versus the Evolution of the TiO_2 content versus the number of points for 30, 60 seconds number of points for 30, 60 seconds



Evolution of the K_2O content versus the Evolution of the MnO content versus the number of points for 30, 60 seconds number of points for 30, 60 seconds

Figure C.12: Evolution of the oxides content versus the number of points for 30, 60 seconds

C.7 RSD for measurement time of 30, 60 seconds



Evolution of the relative standard deviation for *CaO* versus the number of points for 30, 60 seconds



Evolution of the RSD for Al_2O_3 versus the number of points for 30, 60 seconds



Evolution of the RSD for *MgO* versus the number of points for 30, 60 seconds



Evolution of the relative standard deviation for SiO_2 versus the number of points for 30, 60 seconds



Evolution of the RSD for Fe_2O_3 versus the number of points for 30, 60 seconds



Evolution of the RSD for SO_3 versus the number of points for 30, 60 seconds



Evolution of the RSD for P_2O_5 versus the number of points for 30, 60 seconds



Evolution of the RSD for K_2O versus the number of points for 30, 60 seconds



Evolution of the RSD for TiO_2 versus the number of points for 30, 60 seconds



Evolution of the RSD for *MnO* versus the number of points for 30, 60 seconds

Figure C.13: Evolution of the RSD for the oxides versus the number of points for 30, 60 seconds.



Bell curve of CaO oxide for 12 points



Bell curve of CaO oxide for 27 points



Bell curve of CaO oxide for 36 points



Bell curve of *CaO* oxide for 54 points

Figure C.14: Bell curves of *CaO* oxide for random and reguar patterns.



Bell curve of CaO oxide for 15 points



Bell curve of CaO oxide for 29 points



Bell curve of CaO oxide for 48 points



C.8 Acquisition pattern for oxide



Bell curve of SiO_2 oxide for 12 points



Bell curve of SiO_2 oxide for 27 points



Bell curve of SiO_2 oxide for 36 points



Bell curve of SiO_2 oxide for 54 points

Figure C.14: Bell curves of SiO_2 oxide for random and reguar patterns.



Bell curve of SiO_2 oxide for 15 points



Bell curve of SiO_2 oxide for 29 points



Bell curve of SiO_2 oxide for 48 points





Bell curve of Al_2O_3 oxide for 12 points



Bell curve of Al_2O_3 oxide for 27 points



Bell curve of Al_2O_3 oxide for 36 points



Bell curve of Al_2O_3 oxide for 54 points





Bell curve of Al_2O_3 oxide for 15 points



Bell curve of Al_2O_3 oxide for 29 points



Bell curve of Al_2O_3 oxide for 48 points



109



Bell curve of Fe_2O_3 oxide for 12 points



Bell curve of Fe_2O_3 oxide for 27 points



Bell curve of Fe_2O_3 oxide for 36 points



Bell curve of Fe_2O_3 oxide for 54 points





Bell curve of Fe_2O_3 oxide for 15 points



Bell curve of Fe_2O_3 oxide for 29 points



Bell curve of Fe_2O_3 oxide for 48 points





Bell curve of MgO oxide for 12 points



Bell curve of MgO oxide for 27 points



Bell curve of MgO oxide for 36 points







Bell curve of MgO oxide for 29 points



Bell curve of MgO oxide for 48 points





Bell curve of MgO oxide for 72 points

Figure C.14: Bell curves of *MgO* oxide for random and reguar patterns.



Bell curve of SO₃ oxide for 12 points



Bell curve of SO3 oxide for 27 points



Bell curve of SO_3 oxide for 36 points



Bell curve of SO₃ oxide for 54 points

random * 1.0 regular Density of probability 0.8 0.6 0.4 0.2 0.0 2.0 2.5 0.5 1.0 1.5 3.0 3.5 4.0 weight percentage (%)

Bell curve of SO_3 oxide for 15 points



Bell curve of SO₃ oxide for 29 points



Bell curve of SO_3 oxide for 48 points



Bell curve of SO₃ oxide for 72 points

Figure C.14: Bell curves of SO_3 oxide for random and reguar patterns.



Bell curve of P_2O_5 oxide for 12 points



Bell curve of P_2O_5 oxide for 27 points



Bell curve of P_2O_5 oxide for 36 points



Bell curve of P_2O_5 oxide for 54 points

Figure C.14: Bell curves of P_2O_5 oxide for random and reguar patterns.



Bell curve of P_2O_5 oxide for 15 points



Bell curve of P_2O_5 oxide for 29 points



Bell curve of P_2O_5 oxide for 48 points





Bell curve of TiO_2 oxide for 12 points



Bell curve of TiO_2 oxide for 27 points



Bell curve of TiO_2 oxide for 36 points



Bell curve of TiO_2 oxide for 54 points

Figure C.14: Bell curves of TiO_2 oxide for random and reguar patterns.



Bell curve of TiO_2 oxide for 15 points



Bell curve of TiO_2 oxide for 29 points



Bell curve of TiO_2 oxide for 48 points





Bell curve of K_2O oxide for 12 points



Bell curve of K_2O oxide for 27 points



Bell curve of $K_2 O$ oxide for 36 points



Bell curve of K_2O oxide for 54 points





Bell curve of K_2O oxide for 15 points



Bell curve of K₂O oxide for 29 points



Bell curve of K_2O oxide for 48 points





Bell curve of MnO oxide for 12 points



Bell curve of MnO oxide for 27 points



Bell curve of MnO oxide for 36 points



Bell curve of MnO oxide for 54 points

Figure C.14: Bell curves of *MnO* oxide for random and reguar patterns.



Bell curve of *MnO* oxide for 15 points



Bell curve of MnO oxide for 29 points



Bell curve of *MnO* oxide for 48 points


C.9 Moisture impact



Curve of the impact of moisture on CaO



Curve of the impact of moisture on Al_2O_3



Curve of the impact of moisture on MgO



Curve of the impact of moisture on SiO_2



Curve of the impact of moisture on Fe_2O_3



Curve of the impact of moisture on SO_3





Curve of the impact of moisture on P_2O_5

Curve of the impact of moisture on TiO_2



Curve of the impact of moisture on K_2O Curve of the impact of moisture on MnO

Figure C.15: Curves of the impact of moisture on the different oxides.

C.10 Number of points



Curve of the moisture impact on *CaO* with the corresponding SE area.



Curve of the moisture impact on Al_2O_3 with the corresponding SE area.



Curve of the moisture impact on *MgO* with the corresponding SE area.



Curve of the moisture impact on SiO_2 with the corresponding SE area.



Curve of the moisture impact on Fe_2O_3 with the corresponding SE area.



Curve of the moisture impact on SO_3 with the corresponding SE area.



Curve of the moisture impact on P_2O_5 with the corresponding SE area.



Curve of the moisture impact on K_2O with the corresponding SE area.



Curve of the moisture impact on TiO_2 with the corresponding SE area.



Curve of the moisture impact on MnO with the corresponding SE area.

Figure C.16: Curve of concrete tested in dry and wet condition with the standard error area plotted on the curve representing the wet condition.

C.11 Surface carbonation





Figure C.17: Curves of the impact of surface carbonation on the different oxides

C.12 Guideline



Figure C.18: Reason to flip the cube on the left.



Figure C.19: Guideline of the experiments led with the hXRF and SEM-EDS.

C.13 Reproducibility

C.13.1 Comparison of CEM I-based concrete



Test of the reproducibility with two cubes of CEM I-based concrete for *CaO*



Test of the reproducibility with two cubes of CEM I-based concrete for Al_2O_3



Test of the reproducibility with two cubes of CEM I-based concrete for *MgO*



Test of the reproducibility with two cubes of CEM I-based concrete for SiO_2



Test of the reproducibility with two cubes of CEM I-based concrete for Fe_2O_3



Test of the reproducibility with two cubes of CEM I-based concrete for SO_3



Test of the reproducibility with two cubes of CEM I-based concrete for P_2O_5



Test of the reproducibility with two cubes of CEM I-based concrete for K_2O



Test of the reproducibility with two cubes of CEM I-based concrete for TiO_2



Test of the reproducibility with two cubes of CEM I-based concrete for MnO

Figure C.20: Test of the reproducibility with two cubes of CEM I-based concrete

C.13.2 Comparison of CEM I-based concrete with mixes containing 10% GGBFS and 10% FA



Comparison between the two CEM I cubes and the cubes containing 10% GGBFS and 10%FA for *CaO*



Comparison between the two CEM I cubes and the cubes containing 10% GGBFS and 10%FA for Al_2O_3



Comparison between the two CEM I cubes and the cubes containing 10% GGBFS and 10%FA for MgO



Comparison between the two CEM I cubes and the cubes containing 10% GGBFS and 10%FA for SiO_2



Comparison between the two CEM I cubes and the cubes containing 10% GGBFS and 10%FA for Fe_2O_3



Comparison between the two CEM I cubes and the cubes containing 10% GGBFS and 10%FA for SO_3



Comparison between the two CEM I cubes and the cubes containing 10% GGBFS and 10%FA for P_2O_5



Comparison between the two CEM I cubes and the cubes containing 10% GGBFS and 10%FA for K_2O



Comparison between the two CEM I cubes and the cubes containing 10% GGBFS and 10%FA for TiO_2



Comparison between the two CEM I cubes and the cubes containing 10% GGBFS and 10%FA for *MnO*

Figure C.21: Comparison between the two CEM I cubes and the cubes containing 10% GGBFS and 10% FA

C.14 Impact of the aggregates grading



Impact of the grading of the aggregates on *CaO*



Impact of the grading of the aggregates on Al_2O_3



Impact of the grading of the aggregates on MgO



Impact of the grading of the aggregates on SiO_2



Impact of the grading of the aggregates on Fe_2O_3



Impact of the grading of the aggregates on SO_3



Impact of the grading of the aggregates on P_2O_5



Impact of the grading of the aggregates on K_2O



Impact of the grading of the aggregates on TiO_2



Impact of the grading of the aggregates on MnO

Figure C.22: Impact of the grading of the aggregates.

C.15 Chemical composition for concrete blended mixtures



Weight percentage of *CaO* for all the mixes designed in this thesis



Weight percentage of Al_2O_3 for all the mixes designed in this thesis



Weight percentage of MgO for all the mixes designed in this thesis



Weight percentage of SiO_2 for all the mixes designed in this thesis



Weight percentage of Fe_2O_3 for all the mixes designed in this thesis



Weight percentage of SO_3 for all the mixes designed in this thesis



Weight percentage of P_2O_5 for all the mixes designed in this thesis



Weight percentage of K_2O for all the mixes designed in this thesis



Weight percentage of TiO_2 for all the mixes designed in this thesis



Weight percentage of MnO for all the mixes designed in this thesis

Figure C.23: Weight percentage for all the mixes designed in this thesis.

C.16 Chemical composition for concrete blended mixtures for average of 40 up to 60 points



Weight percentage of *CaO* for all the mixes designed in this thesis



Weight percentage of Al_2O_3 for all the mixes designed in this thesis



Weight percentage of MgO for all the mixes designed in this thesis



Weight percentage of SiO_2 for all the mixes designed in this thesis



Weight percentage of Fe_2O_3 for all the mixes designed in this thesis



Weight percentage of SO_3 for all the mixes designed in this thesis



Weight percentage of P_2O_5 for all the mixes designed in this thesis



Weight percentage of K_2O for all the mixes designed in this thesis



Weight percentage of TiO_2 for all the mixes designed in this thesis



Weight percentage of MnO for all the mixes designed in this thesis

Figure C.24: Weight percentage for all the mixes designed in this thesis.

Bibliography

- [1] C. Meyer. Concrete materials sustainable development in united state. *Columbia University*, 14:203–207, 2004.
- [2] M. Taylor, C. Tam, and D. Gielen. Energy efficiency and co2 emissions from the global cement industry. 50, 2006.
- [3] K. Ramsden. Cement and concrete : the environmental impact. *Princeton University*, 2003.
- [4] H. Yoon, E. Seo, D. Kim, and K. Yang. Efficiency of dry calcination and trituration treatments for removing cement pastes attached to recycled coarse aggregates. *Construction and Building Materials*, 312:125412, 2021.
- [5] A. Vervuurt and A. Bigaj van Vliet. Prolonging the service life of concrete structure.
- [6] A. Hanemaaijer, M. Kishna, H. Brink, and J. Koch. Netherlands integral circular economy 2021. *PBL Netherlands Environmental Assessment Agency*, 4228, 2021.
- [7] M. Nedeljković, J. Visser, B. Šavija, S. Valcke, and E. Schlangen. Use of fine recycled concrete aggregates in concrete: A critical review. *Journal of Building Engineering*, 38:102196, 2021.
- [8] R. K. Dhir, J. de Brito, R. V. Silva, and C. Qun Lye. 14 potential for the recycled aggregate market. pages 585–601, 2019.
- [9] Nen-en 12620+a1 :toeslagmateriaal voor beton. *NNI (Nederlands Normalisatie-instituut)*, pages 1–60, 2008.
- [10] I. Sims, J. Lay, and J. Ferrari. 15 concrete aggregates. In *Lea's Chemistry of Cement and Concrete (Fifth Edition)*, pages 699–778. Butterworth-Heinemann, fifth edition edition, 2019.
- [11] H.A. Heinemann. *Historic concrete: From Concrete Repair to Concrete Conservation*. PhD thesis, 2013.
- [12] M. Nedeljković, N. Tošić, and P. Holthuizen et al. Non-destructive screening methodology based on handheld-xrf for the classification of concrete: cement type-driven separation. 2023.

- [13] V. Bilsen, P. Debergh, L. Meindert, L. Graaf, T. Kallay, I. Laureysens, D. Nelen, H. Pollitt, S. Sørensen, P. Szuppinger, M. van acoleyen, I. Vanderreydt, and J. Vermeulen. *Analysis of certain waste streams and the potential of industrial symbiosis to promote waste as a resource for EU industry: final report.* Publications Office, 2015.
- [14] V. Wildeboer and F. Savini. Circular economy and waste markets: Preliminary study of the construction and demolition waste market and its application for the circular economy. 2019.
- [15] M. Nedeljković, A. Mylonas, V. Wiktor, E. Schlangen, and J. Visser. Influence of sand drying and mixing sequence on the performance of mortars with fine recycled concrete aggregates. *Construction and Building Materials*, 315:125750, 2022.
- [16] M.V.A Florea. Secondary materials applied in cement-based products: treatment, modelling and environment interaction. PhD thesis, 2014.
- [17] C. Zhang, M. Hu, X. Yang, B. Miranda-Xicotencatl, B. Sprecher, F. Di Maio, X. Zhong, and A. Tukker. Upgrading construction and demolition waste management from downcycling to recycling in the netherlands. *Journal of Cleaner Production*, 266:121718, 2020.
- [18] M. Nedeljković, J. Visser, T. G. Nijland, S. Valcke, and E. Schlangen. Physical, chemical and mineralogical characterization of dutch fine recycled concrete aggregates: A comparative study. *Construction and Building Materials*, 270:121475, 2021.
- [19] F. Kaddah, H. Ranaivomanana, O. Amiri, and E. Rozière. Accelerated carbonation of recycled concrete aggregates: Investigation on the microstructure and transport properties at cement paste and mortar scales. *Journal of CO2 Utilization*, 57:101885, 2022.
- [20] F. Colangelo, A. Petrillo, and I. Farina. Comparative environmental evaluation of recycled aggregates from construction and demolition wastes in italy. *Science of The Total Environment*, 798:149250, 2021.
- [21] J. Zhang, C. Poon, Z. Xie, C. Shi, Y. Li, and X. Pan. Influence of carbonated recycled concrete aggregate on properties of cement mortar. *Construction and Building Materials*, 98, 2015.
- [22] J. P. Ingham. 5 Concrete. Academic Press, 2013.
- [23] M. Nedeljković. *Carbonation mechanism of alkali-activated fly ash and slag materials*. PhD thesis, 2019.
- [24] R. Siddique and P. Cachim. *Waste and supplementary materials in concrete: Characterisation, Properties and Applications.* Woodhead publishing, 2018.
- [25] H. Feuerborn. Regulation regarding coal ash utilisation in europe. 37:1928– 1947, 2005.

- [26] P. C.Robinson and M. W. Davidson. Polarized microscope. *MicroscopyU*, 2018.
- [27] N. Mostafa. Stabilization and comparison of manufacturing technologies for production of nano-crystalline suspensions. *Chemical and Process Engineering*, 2006.
- [28] National research counsil. *chapter 2 Compositional analysis*. DC: The National Academies Press, 2004.
- [29] B. Siva Sai Kiran and S. Raja. A review on inductively coupled plasma optical emission spectrometry (icp-oes) with a special emphasis on its applications. 9:44–54, 2017.
- [30] J. W. Olesik. Elemental analysis using icp-oes and icp/ms. *Analytical Chem-istry*, 63:12–21, 1991.
- [31] M. de la Guardia and S. Armenta. Chapter 6 multianalyte determination versus one-at-a-time methodologies. In M. De La Guardia and S. Armenta, editors, *Green Analytical Chemistry*, volume 57, pages 121–156. Elsevier, 2011.
- [32] M. Yao, D. Wang, and M. Zhao. Element analysis based on energydispersive x-ray fluorescence. *Advances in Materials Science and Engineering*, 2015:7, 2015.
- [33] S. Aida, Y. Takimoto, T. Sakumura, K. Matsushita, T. Shoji, N. Kawahara, and K. Tsuji. Large-area imaging by wdxrf analysis and elemental monitoring of the dissolution process of a solid sample. *Bunseki kagaku*, 66:885–892, 2017.
- [34] A. Bonneau, J. Moreau, R. Hancock, and K. Karklins. Archaeometrical analysis of glass beads: potential, limitation, and results. *Beads: Journal of the Society of Bead Researchers*, 26:35–46, 2014.
- [35] L.T. Gibson. Archaeometry and antique analysis | metallic and ceramic objects. In *Encyclopedia of Analytical Science (Second Edition)*, pages 117–123. Elsevier, 2005.
- [36] A. B. Poole and I. Sims. *Concrete petrography : A Handbook of Investigative Techniques, second edition.* CRC Press, 2016.
- [37] R. Kheireddine, L. Özcan, F. Doucet, N. Azami, L. Deshays, A. Lebbardi, and F. Vidal. Rapid analysis of phosphate slurries and pressed pellets using laser-induced breakdown spectroscopy. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 163:105735, 2020.
- [38] M. Leprince, L. Sancey, J. Coll, V. Motto-Ros, and B. Busser. L'imagerie élémentaire par spectroscopie libs: De nouvelles applications en médecine. *médecine/sciences*, 35:682–688, 2019.

- [39] X. Wang, S. Lu, T. Wang, X. Qin, X. Wang, and Z. Jia. Analysis of pollution in high voltage insulators via laser-induced breakdown spectroscopy. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 2020.
- [40] S. Pandhija, N.K. Rai, and A.K. Rai et al. Contaminant concentration in environmental samples using libs and cf-libs. *Applied Physics B*, 98:231–241, 2010.
- [41] H. Kondo, N. Hamada, and K. Wagatsuma. Determination of phosphorus in steel by the combined technique of laser induced breakdown spectrometry with laser induced fluorescence spectrometry. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 64:884–890, 2009.
- [42] J. Mputu Kanyinda, A. Kaniki Tsamala, and J. Baele. Libs technology ad its application: Overview of the different research area. *Journal of Environmental Science and Public Health*, 4, July 2020.
- [43] V.F. Lebedev, M.K. Rabchinskii, M.S. Kozlyakov, D.N. Stepanov, A.V. Shidchenko, N.V. Nikonorov, and A.Ya Vul. Laser-induced breakdown spectroscopy: an advanced method for analysis of nanocarbon materials chemical composition. *Journal of analytical Spectrometry*, 33, January 2018.
- [44] V. Motto-Ros, A. S. Koujelev, G. R. Osinki, and A. E. Dudelzak. Quantitative multi-elemental laser induced breakdown spectroscopy using artificial natural networks. *Journal of the European Optical Society, Rapid publication*, 3, 2008.
- [45] B. Lemière. A review of pxrf (field portable x-ray fluorescence) applications for applied geochemistry. *Journal of Geochemical Exploration*, 188:350– 363, 2018.
- [46] X. Zhang, A. J. Specht, E. Wells, M. G. Weisskopf, J. Weuve, and L. H. Nie. Evaluation of a portable xrf device for in vivo quantification of lead in bone among a us population. *Science of The Total Environment*, 753:142351, 2021.
- [47] A.E. Steiner, R.M. Conrey, and J.A. Wolff. Pxrf calibrations for volcanic rocks and the application of in-field analysis to the geosciences. *Chemical Geology*, 453:35–54, 2017.
- [48] D. Smith. Handheld x-ray fluorescence analysis of renaissance bronzes: practical approaches to quantification and acquisition. *Handheld XRF for art and archaeology*, pages 37–74, 2012.
- [49] T. Radu and D. Diamond. Comparison of soil pollution concentrations determined using aas and portable xrf techniques. *Journal of Hazardous Materials*, 171:1168–1171, 2009.
- [50] R. N. Brent, H. Wines, J. Luther, N. Irving, J. Collins, and B. L. Drake. Validation of handheld x-ray fluorescence for in situ measurement of mercury in soils. *Journal of Environmental Chemical Engineering*, 5:768–776, 2017.

- [51] J. Martin, D. Sackett, and C.T. Hays. X-ray fluorescence in the field. *Advanced materials process*, 2005.
- [52] Silicon drift detectors explained. 2012.
- [53] C. Adams, C. Brand, M. Dentith, M. Fiorentini, S. Caruso, and M. Mehta. The use of pxrf for light element geochemical analysis: a review of hardware design limitations and an empirical investigation of air, vacuum, helium flush and detector window technologies. *Geochemistry: Exploration, Environment, Analysis*, 20:366–380, 2020.
- [54] M. Cameron and D. Lehmpuhl C. Burand. Determination of heavy metals in plants with portable xrf. *Resources, Conservation and Recycling*, 2019.
- [55] A.H Pinto. Portable x-ray fluorescence spectrometry : Principles and applications for analysis materials. 2018.
- [56] P. van den Berg, H.W. Corporaal, H.G.A Kouwenhowen, H.H.M. Soen, J.Talsma, T.E.A.C de Veer, R.T de Vree, and K.wiersma. Verdieping beton technology. 2015.
- [57] M. Bijleveld and M. Beeftink. Klimaatimpact van betongebruik in de nederlandse bouw : Vergelijking 1990, 2010 en 2017. September 2020.
- [58] F. de Mendonca Filhoand F., Morillasand H., Derluynand H., Maguregui, M., and Grégoire. In-situ versus laboratory characterization of historical site in marine environment using x-ray fluorescence and raman spectroscopy. *Microchemical Journal*, 147, 2019.
- [59] P. C. Taylor and H. Ceylan E. Yurdakul. Application of a portable x-ray fluorescence technique to assess concrete mix proportion. *National Concrete Pavement Technology Center*, 2012.
- [60] A. Gaddal Falih. Absportion and enhancement correction using xrf analysis of some chemical samples. 1996.
- [61] B.J. Inkson. 2 scanning electron microscopy (sem) and transmission electron microscopy (tem) for materials characterization. In *Materials Characterization Using Nondestructive Evaluation (NDE) Methods*, pages 17–43. 2016.
- [62] G. Hall, G. Bonham-Carter, and A. Buchar. Evaluation of portable x-ray fluorescence (pxrf) in exploration and mining: Phase 1, control reference materials. *Geochemistry: Exploration, Environment, Analysis*, 14:99–123, 2014.
- [63] E. Yundakul, P. C. Taylor, and H. Ceylan. The application of x-ray fluorescence to assess proportions of fresh concrete. 2012.
- [64] P. J. Potts and M. Sargent. In situ measurements using hand-held xrf spectrometer: a tutorial review. 37, 2022.
- [65] S. Fennis. Design of ecological concrete by particle packing optimization. 2010.

- [66] V. Laperche and B. Lemière. Possible pitfalls in the analysis of mineral and loose materials by portable xrf, and how to overcome them. *Institute of Mineral Resources Engineering, RWTH Aachen University*, 2021.
- [67] N. Augusto Rosin, J. A.M. Demattê, M. Cunha Almeida Leite, H. W. Pereira de Carvalho, A. C. Costa, L. T. Greschuk, N. Curi, and S. H. Godinho Silva. The fundamental of the effects of water, organic matter, and iron forms on the pxrf information in soil analyses. *Catena*, 210, 2022.
- [68] T. Quiniou and V. Laperche. An assessment of field-portable x-ray fluorescence analysis for nickel and iron in laterite ore (new caledonia). 14:245– 255, 2014.
- [69] C. Parsons, E. Margui Grabulosa, E. Pili, G. H. Floor, G. Roman-Ross, and L. Charlet. Quantification of trace arsenic in soils by field-portable x-ray fluorescence spectrometry: Considerations for sample preparation and measurement conditions. *Journal of Hazardous Materials*, 262:1213–1222, 2013.
- [70] D. Bernard. History of x-rays 125 yers in the making : part 2 x-rays tubes. 2020.
- [71] L. Baker, I. A. Cristea, T. M. Errington, K. Jaśko, W. Lusoli, C. J. MacCallum, V. Parry, C. Pérignon, T. Šimko, and C. Winchester. Reproducibility of scientific results in the eu: scoping report. 2020.
- [72] E.K. Towett, K.D. Shepherd, and B.L. Drake. Plant elemental composition and portable x-ray fluorescence(pxrf) spectroscopy: quantification under different analytical parameters. 45:117–124, 2015.
- [73] A. Bourke and P.S. Ross. Portable X-ray fluorescence measurements on exploration drill-cores: comparing performance on unprepared cores and powders for 'whole-rock' analysis. *Geochemistry: Exploration, Environment, Analysis*, 16:147–157.
- [74] Oğuzhan Çoporoğlu. Ctb2000: Designing and proportioning design mixtures. 2014-2015.