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Determining alkali content in ASR performance-tested concrete

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Summary

Alkali silica reaction (ASR) is a common deterioration mechanism of concrete. During ASR, reactive aggregate containing silicon oxide (SiO_2) can react with the alkaline fluid in the concrete pores. To test whether a concrete mix is prone to ASR, several concrete prism tests (CPT) have been developed. Performance tests are defined as a CPT where the alkali content in the concrete is comparable to that of a conventional concrete. During CPT, leaching or ingress of alkalis can affect the result of the test, as proven by Lindgård et al. (2013b). However, Lindgård measured leaching and ingress by testing the alkali content in the leachate, lining and wrapping in the test container, but not the prisms themselves.

In my master thesis project, I have investigated four concrete prisms that have been tested with different performance tests. The prisms had experienced different degrees of leaching or ingress according to Lindgårds measurements. The prisms were cut and ground to give concrete powder samples that I tested using cold water extraction (CWE) and hot acid extraction (HAE). Aggregates were also ground and tested with these methods to account for the alkali contribution from the aggregates during CWE and HAE. All samples were tested with thermogravimetric analysis (TGA) to investigate the paste content. CWE and HAE produced solutions which were measured for alkali content using inductively coupled plasma mass spectrometry (ICP-MS). The results were compared to the expected alkali content in the prisms given from the alkali content in the cement from the recipe, minus the measured leaching or ingress. I have investigated all measurements and calculations, and calculated the error based on these. The calculations of errors are based on the principle of error propagation, and I assumed all errors to be uncorrelated.

My results show that HAE is not suitable for measuring the total alkali content, possibly due to the high influence of the aggregates contribution. CWE does not measure the 50-60% of the expected alkali content as reported by Plusquellec et al. (2017), but gives consistent results that are less affected by the contribution from aggregates. Leaching and ingress is indicated in the bulk samples, but the ground profiles do not give any conclusive evidence because of alkali redistribution due to drying during storage. However, transportation of alkali from the top of the prisms to the bottom is indicated, as well as leaching in the top and bottom surfaces of the prisms. Because I have not been able to measure the total alkali content with HAE, I am not able to prove alkali release from aggregates. For a future study XRF could be used for this.

Sammendrag

Alkali-silika reaksjoner (ASR) er en kjent nedbrytningsmekanisme i betong. ASR kan utvikles ved at reaktive tilslag som inneholder silisiumdioksid (SiO_2) reagerer med den alkaliske væsken i betongporene. For å teste hvorvidt en gitt betongmiks er i faresonen for å utvikle ASR er det utviklet flere betongprismetester (CPT). Performancetester er definert som en CPT der man tester betong med et lignende alkali-innhold som i konvensjonell betong. Utvasking eller inntrengning av alkalier kan påvirke en CPT, som påvist av Lindgård et al. (2013b). Lindgårds beregninger er gjort basert på alkalil-målinger av vannet, liningnen og wrappingen i testcontaineren, ikke betongprismene i seg selv.

I masteroppgaven har jeg undersøkt fire betongprismer som er testet med forskjellige performancetester. Prismene hadde ulike grader av utvasking eller inntrenging av alkalier ifølge Lindgårds målinger. Prismene ble kuttet og frest til pulver før det ble testet med cold water extraction (CWE) og hot acid extraction (HAE). Tilslaget ble også knust til pulver og testet med de samme metodene for å redegjøre for bidraget fra tilslag under CWE og HAE. Alle prøver ble testet med thermogravimetric analysis (TGA) for å undersøke pastainnholdet. I løsningene produsert med CWE og HAE ble alkali-innholdet målt med inductively coupled plasma mass spectrometry (ICP-MS). Resultatene ble sammenlignet med det forventede alkalil-innholdet i prismene fra resepten, minus det målte alkali-innholdet som er blitt utvasket eller inntrengt. Jeg har beregnet feilkilder basert på prinsippet om feilforplantning, og har antatt at feilkildene ikke korrelerer.

Resultatene viser at HAE ikke kan benyttes til å måle totalt alkali-innhold, dette kan skyldes at bidraget fra tilslag er stort. CWE måler ikke 50-60% av forventet alkali-innhold som rapportert av Plusquellec et al. (2017), men gir konsistente resultat som er mindre påvirket av bidraget fra tilslag. Utvasking og inntrengning er indikert i bulk-prøvene, mens de freste profilene ikke gir noen bevis på grunn av redistribuering av alkaliene forårsaket av uttørking under lagring. Transport av alkalier fra topp til bunn er indikert, samt utvasking fra topp- og bunn-flaten på prismene. Da jeg ikke har kunnet måle det totale alkali-innholdet med HAE, kan jeg ikke bevise alkali-utslipp fra tilslag. For en fremtidig studie kan XRF bli benyttet til å måle totalt alkali innhold.

1 Table of Contents

List of figures

List of tables

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I would also like to thank my friends and family for supporting me during my 5 years at NTNU.

Preface

This paper represents the main outcome of my master thesis at NTNU, subject code TKT4920. The master thesis accounts for 30 studiepoeng, (this equals 30 ECTS). The work was done from January to June 2017, during my last semester of the study program Engineering sciences and ICT with main focus on structural engineering at NTNU. This paper is written on the subject concrete technology.

My background in concrete is mainly in structures, but I have some basic background with concrete technology from the subject 'Expert in teamwork' where I was at the Concrete Innovation-'village' organized by professor Stefan Jacobsen. I also have some work experience with concrete technology from working at SINTEF Building and Infrastructure on a project with UHPC (Ultra-High Performance Concrete) in the summer of 2016. I wrote a pre-project for my master thesis (7.5 ECTS) from August to December 2016 on the same subject, this pre-project constitutes the introduction to my master thesis.

I had no experience with alkali-silica reactions before I started the pre-project, and I have used this as an opportunity to prove my ability to learn and critically review a new field. My primary focus during five years at NTNU has been structural design and thus this project has been a great opportunity for me to broaden my perspective and make me a more complete structural engineer.

I presented some results from my master thesis at the 7th meeting of the RILEM Technical Committee 258-AAA in Stockholm on May 11th and 12th 2017. The title of my presentation was 'Determining alkali content in performance-tested concrete'.

My supervisors for this project are associate professor Klaartje De Weerdt (main supervisor), postdoctoral fellow Gilles Plusquellec, adjunct professor Børge J. Wigum from NTNU and Heidelberg Cement Northern Europe, and Dr. Jan Lindgård from SINTEF Building and Infrastructure in Trondheim.

1 Background

1.1 Alkali-silica reaction

The alkali-silica reaction (ASR) is a common deterioration mechanism of concrete. During ASR, reactive aggregate containing silicon oxide (SiO_2) can react with the alkaline fluid in the concrete pores.

Alkali metals (sodium (Na^+) and potassium(K^+)) primarily originates from the cement, but a certain amount could potentially come from other sources such as the aggregates. They contribute together with calcium hydroxide from the cement to a high pH in the pore solution. In this thesis, the word alkali refers to alkali metals (Na^+ and K^+) only.

In this high pH environment (normally pH >13) siliceous phases can dissolve in the pore solution, leading to the precipitation of a water-absorbing gel. Over time the gel swells as the concrete is exposed to water/humidity, causing expansion, cracking and later weakening of the concrete's load bearing capabilities (Lindgård et al., 2012). A real-world example of this is the Elgeseter Bridge in Trondheim, where ASR developed. The bridge expanded 0.1% during 50 years of exposure. With a span of 200 m, the bridge deck expanded 20 cm due to ASR over this period of time (Skogli, 2015)

The alkali-silica reaction requires three conditions; reactive aggregates containing reactive silicon oxide, a high concentration of alkalis in the pore solution in order to reach a high pH, and a high level of moisture (water) for the silicon oxide to dissolve into and for the gel to absorb in order to swell. All requirements must be present for ASR to develop. The requirements are presented in Figure 1.

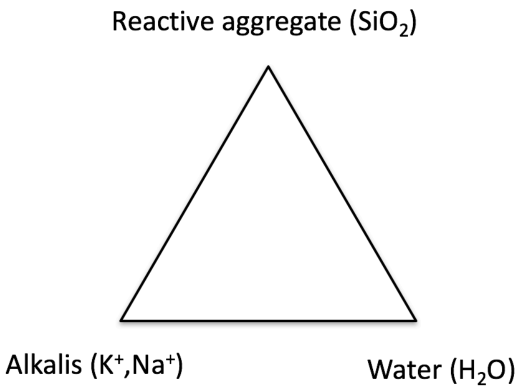

Figure 1, Requirements triangle for ASR (Lindgård, 2007)

1.2 Free and total alkali content

Total alkali content of concrete is calculated as the total alkali content in the cement used in the concrete. This is known from the manufacturer and is given as a percentage of the cement, for example 0,7% alkali content in a cement. When this cement is used in a concrete, with a typical cement quantity of 400 kg cement /m^3 of concrete, this yields 2,8 kg Na_2O_{eq}/m^3 of concrete. As cement is considered the source of total alkali in concrete, total alkali content of the concrete is defined as 2,8 kg Na_2O_{eq}/m^3. The unit, kg Na_2O_{eq} /m^3, where m^3 refers to m^3 of concrete if nothing else is specified, is widely used as a unit for alkali content in concrete, as it is relatively easy to convert concentrations of Na and K into kg Na_2O_{eq}/m^3, this will be presented in chapter 3.1.

Free alkali is defined as the alkali present in the pore solution. The free alkali can originate from the cement itself (dominating source), from the aggregates (in some cases), additives (e.g. plasticizers) or from ingress of alkali from the external environment (e.g. seawater, de-icing salt). The exact percentage of the total alkali present in the pore solution is not known as it depends on a number of variables such as the binder type, water-to-binder ratio, degree of hydration, aggregate type and environment. Plusquellec et al. (2017) found that 50-60% of the total alkali is free in the pore solution for CEM I. The remaining total alkali that is not present in the free alkali is in the hydrate or clinker.

1.3 ASR concrete prism tests

Ever since D. E. Stanton first recognized ASR in 1940 there has been comprehensive studies focused on finding test methods for determining the reactivity of aggregates (Lindgård et al., 2012). The test methods assumed to be most reliable, are defined as concrete prism tests (CPTs). They all consist of casting prisms of the concrete you want to test, expose the prisms to an accelerated environment with high relative humidity (access to water) and elevated temperatures. After a given exposure period the prism expansion is measured. If the expansion is within the acceptance criteria (from regulations), the given aggregate or concrete is approved.

RILEM[1] has developed a series of CPTs, and in North America the ASTM-organization developed similar tests. These tests were developed for testing the aggregates to see if they were reactive by mixing concrete with high alkali cement and expose the concrete prisms in a moist environment. This in order to stress the aggregates (ASTM, 2008) and measure expansion to see if ASR was developed. These tests are known as **aggregate tests**. The reason for using concrete with high alkali content, and not just regular concrete is to accelerate the process, as ASR normally takes years to develop in conventional concrete (with lower alkali content).

Jan Lindgård wrote a PhD published at NTNU in 2013 titled ‘Alkali-silica reaction (ASR) : performance testing’. The main focus of Lindgård’s PhD was to “…evaluate whether concrete prism tests developed for assessment of alkali–silica reactivity of aggregates might be suitable for general ASR performance testing of concrete“ (Lindgård et al., 2012). Lindgård mixed concrete with conventional cement with lower alkali contents in order to see how this normal concrete would react to the tests, this is known as **performance testing**.

Lindgård’s PhD laboratory test program was an extensive study with a total of 58 test series, all using a different variation of four main test methods. The four main test methods were: RILEM AAR-3 (2000), RILEM AAR-4.1 (2006), ASTM C-1293 (2008) and Norwegian 38° CPT (2005). These are presented in Table 1.

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[1] RILEM is an international union of laboratories and experts in construction materials, systems and structures.

Table 1, Test methods as described in Jan Lindgård's PhD (Lindgård et al., 2013a)

Method	Pre-treatment	Temperature (± 2°C)	Prism size (mm^3)	Storage conditions	Measuring intervals (Weeks)	Exposure period (Weeks)	Reference
RILEM AAR-3	Wrapped in damp cloth directly after demolding	38°C	75(±5) x 75(±5) x 250(±50)	Prism wrapped with a cotton cloth added 80g deionized water and stored inside polyethylene bag. The bag is placed on a grid over water in a sealed plastic cylinder with a lining of filter paper. The lower part of the lining is immersed in the deionized water.	2, 4, 13, 26, 52	52	(RILEM, 2000)
RILEM AAR-4.1	Submerged in water for 30 min after demolding	60°C	75(±5) x 75(±5) x 250(±50)	Unwrapped prisms stored in a tight container on a grid over the deionized water. The container is stored in a large tank holding 60°C on a grid over water.	5, 10, 15, 20	20	(RILEM, 2006)
ASTM C-1293	No submersion after demolding	38°C	75 x 75 (no limit on length of prism)	Unwrapped prisms stored in a plastic container with a thick cotton lining, with lower part of lining immersed in the deionized water and the prisms on a grid so they do not touch the water.	1, 4, 8, 13, 26, 39, 52	52	(ASTM, 2008)
Norwegian 38° CPT	Submerged in water for 30 min after demolding before reference readings are taken	38°C	100 x 100 x 450	Unwrapped prisms stored in a plastic container with a thick cotton lining, with lower part of lining immersed in the deionized water and the prisms on a grid so they do not touch the water.	1, 8, 16, 26, 52	52	(Norwegian Concrete Assosiation, 2005)

"Test setups" are in principle the same for all test methods; first concrete prisms are cast, after demolding the prisms undergo different pre-treatments depending on the test method, see Table 1. After pre-treatment the concrete prisms are placed in a tightly sealed container, either one (only RILEM AAR-3 (2000)) or three in the same container depending on the method. Inside the container the prisms are placed on a grid (for example made of plexi glass), so that the prims do not touch the water in the bottom of the container.

In RILEM AAR-3 (2000), ASTM C-1293 (2008) and Norwegian CPT (2005) the walls of the container are covered by a lining in contact with the deionized water on the bottom of the container. This, in order to secure a high relative humidity (RH) in the upper part of the container. Additionally, in RILEM AAR-3 (2000), the prisms themselves are wrapped with a moist cotton cloth in order to increase the access to water. The temperature in these three tests is 38°C.

In RILEM AAR-4.1 (2006), there is no lining. However, the temperature is 60°C.

The prisms in Lindgård's PhD and in subsequent follow-up study WP2 (Lindgård, 2016) had a quadratic cross section measuring 70 mm by 70 mm, and a length of 280 mm. , except for the prisms tested with Norwegian CPT (2005) which were 100 mm by 100 mm and a length of 450 mm. This dimensions are within the limits for both RILEM and Norwegian CPT test procedures, but slightly smaller than the limits for ASTM C-1293 (75 mm).

The prisms selected for the project described in this paper, have all undergone one of four different test procedures described in Lindgård's PhD. Some of these were modified versions of the four main methods see Table 2. These prisms are described more in detail in chapter 2.1.

Table 2, Modified procedures used on the samples selected for this project (Lindgård et al., 2013b)

Method	Based on	Revisions from original test
4.6	RILEM AAR-4.1	Prism is stored submerged in de-ionized water since demolding. Water replaced after each measuring.
3.5	RILEM AAR-3	Unwrapped prism is sealed in epoxy and aluminum foil after demolding, no water in the storage container
3.12	RILEM AAR-3	Prism submerged for 30 min after demolding. The wrapping contains a liquid solution with pH 14.2 from the start instead of deionized water
ASTM	ASTM C-1293	No revisions except for slightly smaller prism cross section (70 mm by 70 mm, instead of 75 mm by 75 mm)

1.4 Alkali leaching

The main focus of the concrete prism test methods is to measure the expansion of the prisms after a given exposure period (see Table 1) under accelerated conditions. If the expansion exceeds the acceptance criterion, the concrete is classified as prone to ASR. In his PhD Lindgård also focused on alkali leaching measurements. Alkali leaching is a phenomenon where alkali is removed from the concrete by water on the concrete surface (Rivard et al., 2003). Leaching in turn reduces the expansion caused by ASR as it removes alkali (and thus reduces the pH in the concrete pore water), one of the three requirements for ASR (see Figure 1).

Lindgård measured alkali leaching at each measuring interval (see Table 1) by extracting 20 ml from the water in the bottom of the storage containers during the exposure period and at the end. The water was extracted from the bottom of the container. The water was stirred before the sample was extracted in order to distribute the alkalis evenly. The volume of the water in the bottom of the container was also measured (Lindgård et al., 2013b).

When collecting the last sample at the end of the exposure period the alkali in any lining or wrapping were also measured by cutting the cloth in smaller pieces and submerging them for a week in a container with 1500 ml of deionized water, and then collect a 20 ml sample. The last sample can be considered as the most accurate measurement of total alkali leaching from the given concrete prisms as this contains the alkali from both the water in the bottom of the container, and the alkali from any lining or wrapping. This is especially true for prisms tested with the AAR-3 method, as these prisms were wrapped. Furthermore, as the water volume during exposure was determined by measuring the height of the water in the bottom of the container, the end of the exposure period presents the opportunity to measure the volume accurately by weighing the water and from this get a more correctly calculated alkali content. All 20 ml samples were stored in alkali-resistant plastic bottles. (Lindgård et al., 2013b)

The alkali concentration (Na, K) of the 20 ml water samples were analyzed with flame spectroscopy. The details on the calculations of alkali leaching from these measurements is given in chapter 3.2.

At exposure temperature 60°C Lindgård found that the amount of alkali leached out during the first 4 weeks of exposure correlated with the ultimate prism expansion. Lindgård found that alkali leaching is the main controlling factor for the prism expansion. Consequently, in order to predict what would happen in a real concrete structure (where alkali leaching should be minor or non-excitant) alkali leaching during performance testing should be minimized. At 38°C the larger 100x100 mm^2 cross section of the Norwegian CPT test method leached less (roughly half) than the 70x70 mm^2 cross sections (Lindgård et al., 2013b).

1.5 Threshold

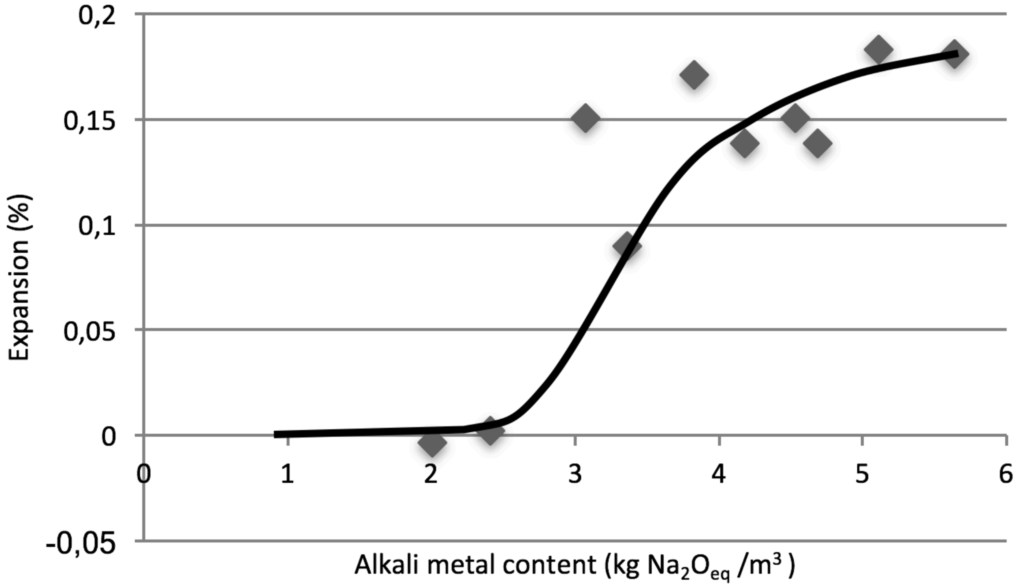

Figure 2, Expansion vs. alkali content for CEM I with Årdal non-reactive aggregate fines and Ottersbo reactive coarse aggregate tested with Norwegian CPT after one year exposure (Lindgård, 2013)

Figure 2 illustrates the background for this research. It shows expansion after one year of prims made with CEM I and Årdal/Ottersbo aggregate and tested with Norwegian CPT. Each data point represents one test series (mean of 3 prisms). The x-axis shows the original alkali content of the cement in the sample and the y-axis gives the expansion. All prisms are made with CEM I cement and Årdal/Ottersbo aggregate, but the alkali content can be increased by adding NaOH in the mixing water and/or mixing high- and low-alkali cement. Adding NaOH is a technique called "boosting". The line is drawn to illustrate how these data points follow a trend. The figure shows that, for a given aggregate the expansion depends on the alkali content of the concrete.

In this study alkali threshold is defined as the alkali content where the expansion increases drastically[2] for a given cement/aggregate combination.

The data points most to the right are from what is defined as **aggregate tests**, as the alkali content is artificially boosted to be very high. The alkali content in aggregate tests are boosted to be much higher than the alkali threshold, hence these are less influenced by alkali leaching. The first two data points on the figure (to the left) come from what would be defined as **performance tests** as these are test series made with cement with low alkali content. As the alkali content for performance tests are close to the alkali threshold, alakli leaching strongly influences expansion, as a small variation of the alkali content affects the expansion significantly.

By boosting prisms and testing them the alkali threshold for a given cement/aggregate combination can be determined.

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[2] Alkali threshold can also be defined as the alkali content where the prism expansion is equal to the critical expansion limit (acceptance criteria) for a given aggregate combination.

In 1996, the Norwegian Concrete Association published a national guideline on ASR called NB 21 (revised in 2004 and translated to English in 2008). It stated, based on laboratory performance testing and field-testing, that the critical alkali content limit for CEM I binders should be 3.0 kg Na_2O_{eq}/m^3 (Norwegian Concrete Norwegian Concrete Assosiation, 2008).

In his PhD test program Lindgård used an alkali content of 3.7 kg Na_2O_{eq}/m^3, on concrete made with CEM I binder, 0.7 kg Na_2O_{eq}/m^3 more than the critical alkali content limit in the Norwegian regulations. This level was chosen based on previous testing to be in the steep part of the expansion/alkali content-curve (see Figure 2), so that the effect of alkali leaching would be easily detected. He found that leaching strongly influences concrete prism expansion, see chapter 1.4. (Lindgård et al., 2013b)

In the 1990's, Canadian scientists examined old dams in the Québec-area affected by ASR. The interesting thing was that many of the dams were built using concrete with alkali content within todays Canadian regulations, CSA A23.1, that sets the critical alkali content limit to between 1.7 and 3.0 kg Na_2O_{eq}/m^3 depending on type of structure and exposure conditions. After drilling cores and extracting free alkali from the cores using hot water extraction (HWE, see chapter on measuring free alkali content) Bérubé et al. (2002) found that the bulk free alkali content of the cores exceeded the expected alkali content of the concrete. After measuring the alkali release from the aggregates by submerging the aggregate particles in water for 578 days they concluded that the additional free alkali must have come from the aggregates themselves. However, the release of alkali from aggregates would happen over time, thus making some aggregates an ASR "time bomb". Lindgård also reported a prism that leached more than 100% of the calculated alkali content of the cement, see chapter 2.1.

The RILEM Technical committee (TC) 258-AAA is currently testing a draft aggregate release test called AAR-8 (Menéndez et al., 2014). This test consists of exposing aggregates in sodium hydroxide (NaOH) and potassium hydroxide (KOH) and measuring released alkali from the aggregates. AAR-8 is currently tested in a round robin test with the RILEM TC where SINTEF Buildings and Infrastructure is a part. SINTEF's preliminary results show massive alkali release, i.e. 6.0 kg Na_2O_{eq}/m^3 for the most extreme aggregates. The test has been designed to compare the release from different types of aggregates. However, as the test conditions are much more aggressive than the actual condition inside concrete, the values have to be adjusted in order to give a realistic release value in concrete. Thus, a verification calculation is needed to make use of this test method. There are ongoing research projects that aim to link results from AAR-8 testing to real alkali release in field concrete.

The question is; how do we find a reasonable critical limit for alkali content to base concrete regulations on when taking leaching from concrete as well as alkali release from aggregate into account?

This is of great interest for cement, aggregate and concrete producers, as new regulations based on rough or even erroneous estimations could constrain concrete producers to use cement with unrealistically low alkali contents, and/or aggregates with low alkali release. This is an issue for the entire construction industry as cement producers would be limited to produce very low alkali cement, aggregate producers only sell aggregates with little or no potential alkali release. This would drive the prices up, limit availability and this is not sustainable.

In order to address this question, we first need to develop reliable performance tests that take both alkali leaching and alkali release from aggregates into account. Lindgård's PhD in part achieves this by proving that leaching and pre-treatment are influencing performance tests, and recommends using bigger prism cross-sections in the tests. However, his measurements of alkali leaching are purely based on measuring alkali content in the leachate, lining and wrapping in the container. These measurements have given some peculiar results. In one prism, he measured more alkali leached from prism than the actual total alkali content of the cement.

In this project I will try and document the alkali content in the concrete prisms themselves.

1.6 Objectives

For my master's thesis, I will work with the following research challenge:

Determine and visualize the alkali content and distribution in concrete prisms that have been performance tested, using cold-water extraction for free alkali and hot acid extraction for total alkali. The results will be compared with the alkali contents in the original mix design minus the leachate in the container, as this should be the alkali remaining in the prism. This should prove alkali leaching or ingress during the concrete prism test. I will also investigate if a part of the measured free alkali content in the prisms is due to release from the aggregates. Finally, this should give a better basis for improving performance tests.

In order to solve this, I have first selected four concrete prisms that have been performance-tested using the concrete prism tests listed in Table 3. The prisms will be further introduced in chapter 2.1. The prisms will be sawn and ground before testing with the cold-water extraction (CWE) method to determine free alkali distribution in the prisms, and the hot acid extraction (HAE) method to determine total alkali distribution in the prisms.

This is done to prove that alkalis have actually leached out of the prisms, and that we can say with certainty that this is a defining factor for reduced expansion. By profile grinding and performing CWE and HAE measurements I will get enough data points to produce plots that is assumed to show less alkali close to the surface than in the core of the prism, proving alkali leaching or ingress. By calculating the theoretical free alkali content from the total alkali content, I should be able to theorize how much alkali is released from the aggregates in each prism.

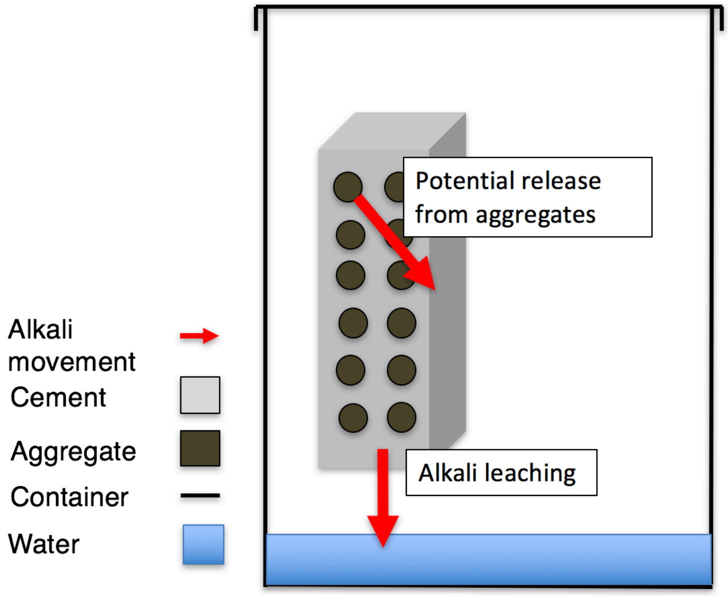

Figure 3, Illustration of alkali movement during concrete prism test

2 Experimental

2.1 Materials

I have chosen four concrete prisms for further investigation in the masters project, two are from Jan Lindgård's PhD (2013) and the other two are from COIN[3] WP 2 performance tests (Lindgård, 2016). The prisms are presented in Table 3 and Figure 4. All prisms are made with the same cement type (CEM I) and the same aggregates, but with slightly different quantities of aggregates, see the recipes in Table 4.

The first two prisms represent extremes from Lindgård's PhD laboratory tests.
The first prism, I will call this prism E (Epoxy), is a reference prism, as it was sealed with epoxy before it was stored using the 3.5 test procedure, an alternative version of the AAR-3 test, see Table 2. Lindgård presents that no alkali leaching occurred due to storage in a dry container. Prism E is a reference of how a prism would appear if no leaching had taken place.

The second prism, I will call prism S (Submerged), was exposed to the 4.6 test procedure, an alternative version of AAR-4.1, see Table 2. Lindgård's measurements of alkali in the water in the container show that this prism has leached more alkali than the calculated total alkali content of the cement. Therefore, this prism has been studied for two reasons; to prove that alkali leaching has occurred and, if there still are alkalis present in the concrete pore water, do they originate from the aggregates?

The two last prisms, I will call prism A and W, originate from COIN WP2. They are made with the same aggregate as the two benchmark prisms (E and S), but with a slightly different quantity of aggregates, as per the recipe in Table 4.

Prism A (ASTM) was tested with the ASTM C-1293 test procedure, and based on measured alkali in the containerthe alkali content is reduced from the original 2.8 kg Na_2O_{eq} /m^3 to 3.88 kg Na_2O_{eq} /m^3 or 50.7% alkali leaching.

Prism W (Wrapped) has been tested with the AAR-3.12 test procedure, an alternative version of AAR-3, see Table 2. Because of the test method the prism had most likely experienced the opposite of leaching, i.e. an ingress of alkali. The measured alkali content in the container show that the alkali content has increased in the prism from the original 2.8 kg Na_2O_{eq} /m^3 to 3.88 kg Na_2O_{eq} /m^3 or 38.5% alkali ingress.

The aggregates used in the prisms were Årdal fines and Ottersbo coarse. Årdal is a non-reactive natural aggregate containing granite, and Ottersbo is the most reactive aggregate in Norway, it is a cataclasite. The aggregates themselves were also tested for alkali content. It is important to note that we tested "fresh" aggregates that had not been cast in concrete before testing.

All samples have been tightly wrapped in a thick plastic film and sealed with tape after exposure. They have been stored dry and at room temperature in the SINTEF lab.

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[3] COIN (Concrete innovation center) was a center for research-based innovation between 2007 and 2014. https://www.sintef.no/en/projects/coin/

Table 3, Prisms tested in MSc project, illustrated in Figure 4

Name	Origin	Test method (see Table 2)	Cement	Aggregate (fine/coarse)	Recipe	Cement alkali content (kg Na_2O_{eq}/m^3)	Resulting alkali content after exposure[4] (kg Na_2O_{eq}/m^3)	Leaching / Ingress (-)	Expansion / Shrinkage(-)	Year of casting
E (Epoxy)	JL PhD	3.5 based on AAR-3 38°C	CEM I	Årdal / Ottersbo	I	3.7	3.7	0%	(-0.02)%	2008
S (Submerged)	JL PhD	4.6 based on AAR-4.1 60°C	CEM I	Årdal / Ottersbo	I	3.7	0.0	>100%	0.02%	2008
A (ASTM)	COIN WP2	ASTM C-1293	CEM I	Årdal / Ottersbo	II	2.8	1.38	50.7%	~0,08%	2011
W (Wrapped)	COIN WP2	3.12 based on AAR-3 38°C	CEM I	Årdal / Ottersbo	II	2.8	3.88	(-38.5)%	~0,47%	2011

Table 4, Nominal concrete recipes

	I	II
Cement	400 kg/m^3	400 kg/m^3
Årdal agg.	735 kg/m^3	698.5 kg/m^3
Ottersbo agg.	1098 kg/m^3	1045 kg/m^3
Water	183 kg/m^3	183 kg/m^3

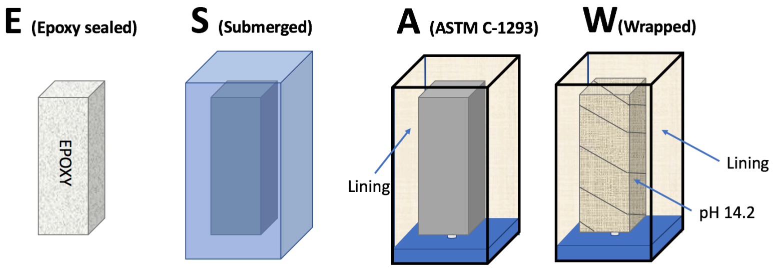

Figure 4, Illustration of prisms

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[4] Based on alkali leaching measurements

2.2 Methods

This chapter presents where the samples tested with Cold water extraction (CWE) and Hot acid extraction (HAE) originate from in the prisms. An overview of this is presented in Figure 5. Further I present the two methods I used to measure alkali content in the prisms; CWE and HAE.

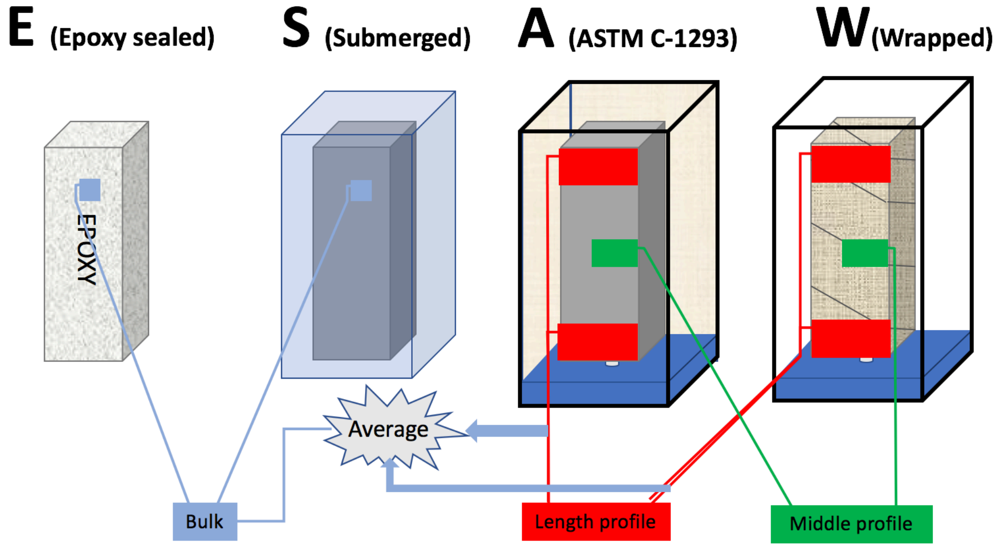

Figure 5, Overview of grinding of prisms

2.2.1 Prism E and S

As prism E and S were measured to have 100% leaching and no leaching respectively, I expect the alkali distribution to be even in both prisms, and therefore a single bulk sample was ground.

2.2.1.1 Bulk grinding

The bulk sample was collected by grinding a sample in the middle of the prism approximately 2 cm from the top. The sample was ground at the SINTEF lab. To ensure that the entire sample met the require particle size, it was sieved first, and then the part that did not go through the sieve was ground using a mortar.

2.2.2 Prism A and W

As prism A and W had experienced leaching and ingress respectively according to the measurements made by Lindgård, the alkali distribution was expected to be less even than in prism E and S, therefore I had the prisms cut and ground in the middle, top and bottom to try to visualize the distribution.

2.2.2.1 Concrete sample cutting

The 280 mm x 70 mm x 70 mm prisms (A and W) were sawn into three parts. Two 115 mm x 70 mm x 70 mm prism were sawn from the top (I will call this sub-prism 1) and bottom (sub-prism 3). A 50 mm x 70 mm x 70 mm prim (sub-prism 2) remained from the middle part of the original prism, see Figure 6**Error! Reference source not found.**.

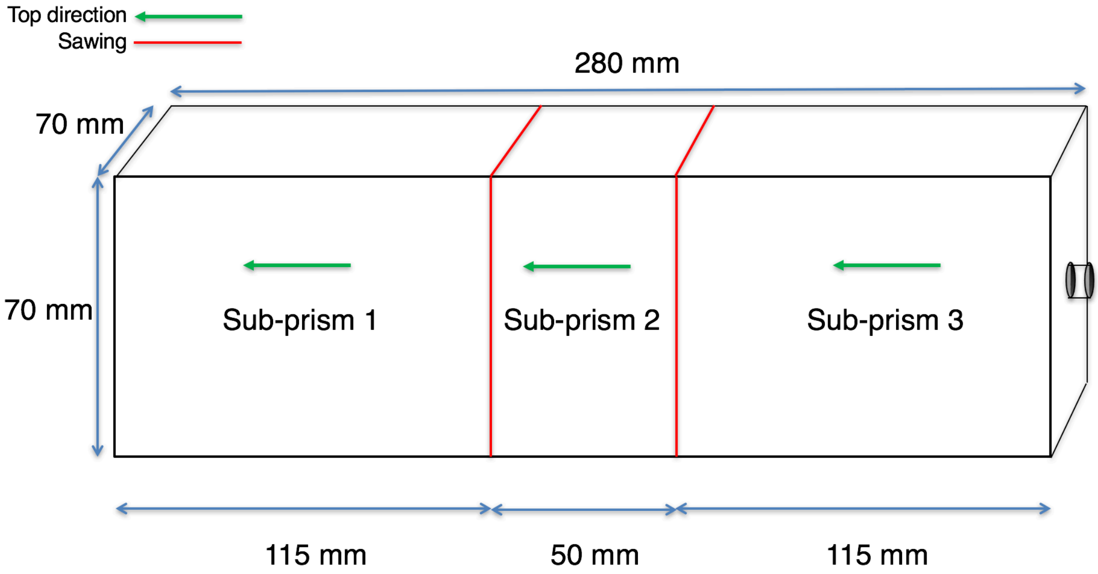

Figure 6, Sawing of prisms A and W

2.2.2.2 Length profile grinding

Sub-prisms 1 and 3 were ground in 3 steps of 20 mm from the top and the bottom respectivly, a total of 6 data points per prism (see Figure 7). After testing these with CWE and HAE, the average of all 6 samples was considered as a representative of the bulk sample, see Figure 5. The 6 samples represent a length profile to see the difference in alkali distribution in the top and bottom as the prism were stored with the same side up during the exposure period.

The samples were cut and ground at the SINTEF lab. However, the entire sample did not meet the required 80 µm powder particle size requirement, but approximately 50% did. To ensure that the entire sample met the require particle size, it was sieved, and then the part that did not go through the sieve was ground with a vibratory disk mill. The model used in this study was a RS 200 from Retsch. The part of the sample with particle size >80 µm was ground for 30 seconds with 1500 rpm and then sieved on a 80 µm sieve to confirm that the particle size was correct.

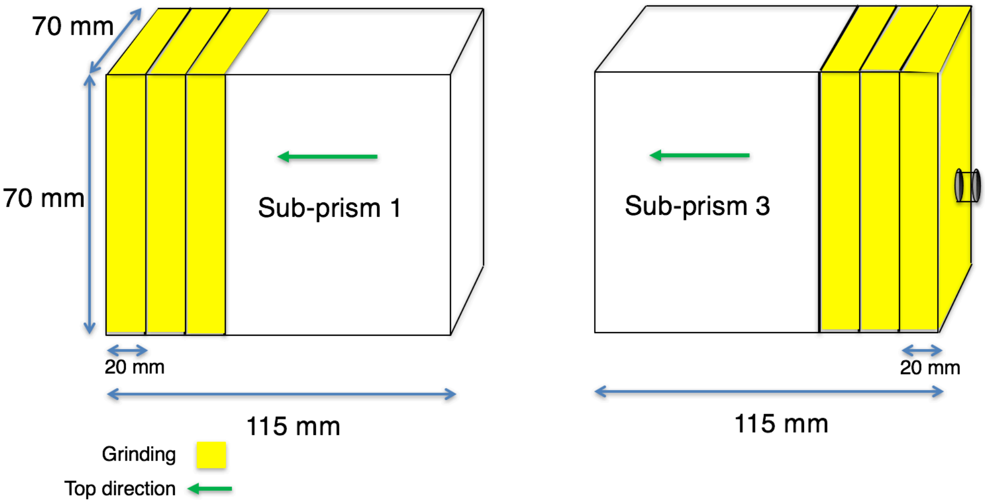

Figure 7, Length profile grinding, prisms A and W

2.2.2.3 Middle profile grinding

To visualize the free alkali content distribution from the middle of the prism to the surface, a middle profile is ground with 3 mm steps into the center of the prism. As the cuts in the middle profile are much smaller than the bulk and length profile, the wall effect[5] must be considered.

Leaching must also be taken into consideration as this is a three-dimensional object, and it will have leached equally on all sides. Therefore, removing the outer layer on two opposite sides should provide a better two-dimensional cut of the sample.

To minimize the wall effect 10 mm was sawn from the two opposing ends, Figure 9.

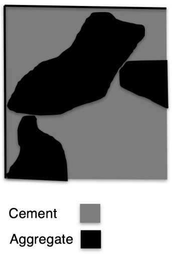

Figure 8, Wall effect

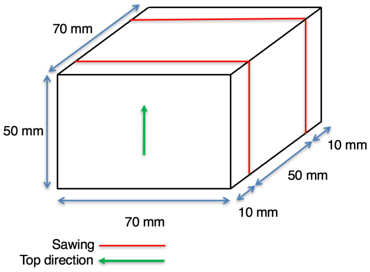

Figure 9, Schematic sawing plan for minimizing wall effect for sub-prism 2.

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[5] Samples with aggregates (fine or coarse) normally have a lower aggregate content near the surface because of the mould (Zheng and Li, 2002). This is known as a skin or wall effect (Figure 8). This might be problematic for consistent CWE results, as the cement paste content preferably should be the same. The samples were also tested with TGA to investigate variations in paste content

On the remaining part of sub-prism 2, measuring 50 mm x 50 mm x 100 mm, 3 mm is ground from the 50 mm x 50 mm cross section. The grinding was made with a profile grinder at the SINTEF lab. This ground concrete represents one data point that will be analyzed for free alkali content using CWE. The minimum amount of powder we need for CWE is 10 g. If we calculate with a concrete density of 2400 kg/m^3 each of the ground samples should give 18 g of powder, see equation 1.

$$50\ mm * 50\ mm * 3\ mm * 2400\frac{kg}{m^3} * 10^{-6}\frac{g\ m^3}{kg\ mm^3} = 18\ g \qquad [1]$$

This is repeated 11 more times for a total of 12 ground concrete samples, this procedure is called profile grinding, see Figure 10. 12 data points was taken to reach the center of the cross section. Because the free alkali distribution is expected to be symmetrical, samples are only taken from one side.

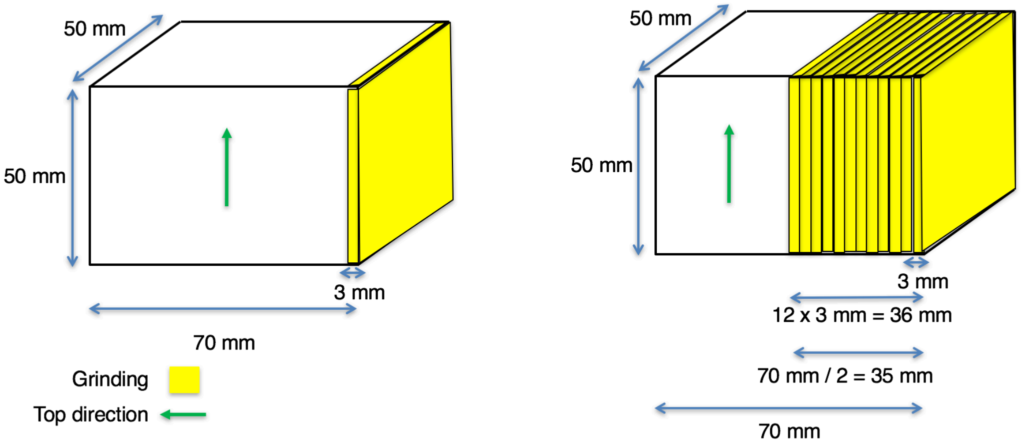

Figure 10, Profile grinding, prisms A and W

The resulting powder did not meet the required particle size of 80 µm. Because the quantity of material obtained was small, the samples were ground in a mortar before testing to meet the requirement.

2.2.3 Aggregate sample preparation

For analysing the aggregates by CWE and HAE, the aggregates were ground to a <80 µm powder. This was done with the vibratory disk mill. The aggregates were ground for 30 seconds at 1500 rpm and then sieved on an 80 µm sieve to confirm that the particle size requirement was met.

2.2.4 Sample storage

All the ground samples were stored in labelled bags in a desiccator containing soda lime to avoid carbonation.

2.2.5 Cold water extraction

Cold water extraction (CWE) is used to measure the free alkali content of a cement, mortar or concrete sample (Plusquellec et al., 2017).

CWE consist of four steps: (1) grinding the sample to a powder, (2) leaching of the powdered sample in water, (3) separating the liquid from the solid and (4) analysing the extracted solution. See Figure 11 for illustration of the procedure. CWE is also known as ex situ leaching, and has been used in several studies. Although the name states the water is cold, it should be room temperature or about 20°C.
CWE can be done in numerous ways depending on particle size, liquid-to-solid ratio (L/S) and extraction time. Alonso et al. (2012) recommended using a particle size below 80 µm to allow the sample to have a great enough surface, a L/S of 1, and a 5-minute extraction time. This recommendations are used in my study.

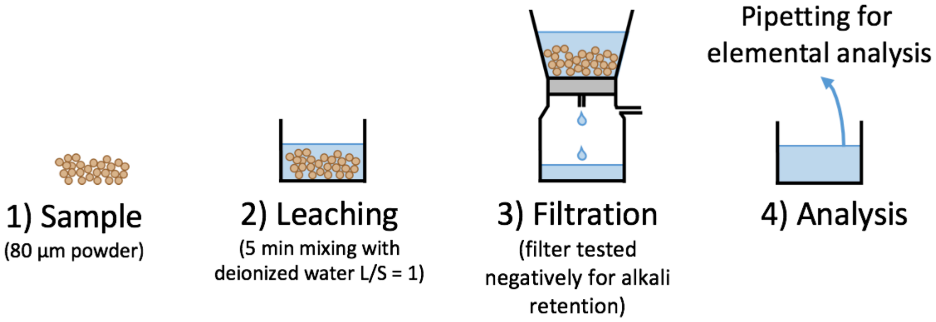

Figure 11, CWE procedure (Plusquellec et al., 2017)

First a precise balance (±0.001 g) is used to weight the sample powder in one beaker and deionized water in another beaker. The powder and water mass was 10 g where this is possible, but never less than 5 g as to ensure a sufficient amount of extracted solution. After weighing the sample powder, the beaker was covered to avoid contamination.

The powder was mixed with the water for 5 minutes using a magnet and a magnetic stirrer.

After 5 minutes, the solution is poured into a filtration unit. The filtration unit consist of a 500 ml Erlenmeyer with a sintered glass filter covered with an 8 µm cellulose filter (grade 40). The filtration unit is connected to a water pump.

The solution was then collected in a vial. The solution needs to be diluted 10 times before analysis to be in the range of the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) thatwas used to measure the amount of alkali in the sample. The diluted sample is acidified with 140 µl of 65% HNO_3 diluted by 2. The mother sample is acidified with 70 µl of the same acid.

Alkali from the aggregates can be released when testing concrete with CWE. Therefore, the aggregates themselves are tested with CWE to correct for this in the calculations. However, this may lead to an overcorrection if the concrete has experienced release of alkali from the aggregates.

2.2.6 Hot acid extraction

To determine the total alkali content, I used a method that I will call Hot Acid Extraction (HAE) in this thesis. This was done to see how much alkali was in the samples, as this should be comparable to the recipe minus the leachate for the prisms. That is, HAE is used to measure the total alkali content in the sample, where CWE measures the free alkali content.

HAE also consist of four steps: (1) Grinding the sample to a powder, (2) dissolving of the powdered sample in hot acid, (3) separating the liquid from the solid and (4) analysing the extracted solution. See Figure 12 for an illustration of the procedure.

5 g of the powdered sample (with particles size <80 µm) is added to a 100 ml beaker with 40 ml of 10 times diluted 65% HNO_3.

A heater keeps a 1000 ml flat beaker filled with deionized water at 80 °C, this will act as a water bath. The 100 ml beaker with the acid and powder is put into the hot water. The acid and powder is gently stirred with a glass rod to dissolve the sample for one hour.

After one hour, liquid is filtrated from the solid using the same filtration unit as used for CWE.

The sample liquid was diluted 20 times to be in the range of the ICP-MS.

For the length profile samples from prism A and W HAE was done for me at SINTEF. The procedure was the same, but 50 ml of acid were used and the solution was diluted 10 times.

Alkali from the aggregates will be released when testing concrete with HAE. Therefore, the aggregates themselves were also tested with HAE to correct for this.

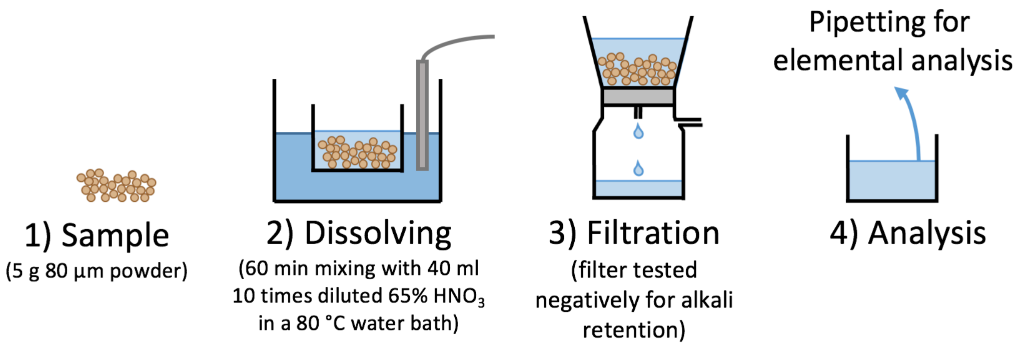

Figure 12, HAE procedure

2.2.7 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

The diluted filtrate from the CWE and HAE was analyzed for concentration of Na and K with inductively coupled plasma mass spectrometry (ICP-MS) using an Element 2 ICP-MS from ThermoFisher Scientific. ICP-MS yields the results in µg/L of solution.

2.2.8 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was used to investigate the paste and aggregate content in the powdered samples to determine if they were representative of the entire prism. TGA is used to analyze cement paste content by quantification of portlandite ($Ca(OH)_2$) and water. Using known ratios between portlandite and cement, the amount of aggregates in the sample can be calculated from the TGA results.

For the middle profiles in prisms A and W (sub-prism 2), TGA analysis was performed on the four outer samples and every other into the center (see Figure 13). The detailed TGA in the outer layer is to get a detailed profile where the wall effect is the greatest. For the length profile in prisms A and W (sub-prism 1 and 3), TGA was performed on all samples. TGA was performed on the bulk samples from the prisms E and S as well.

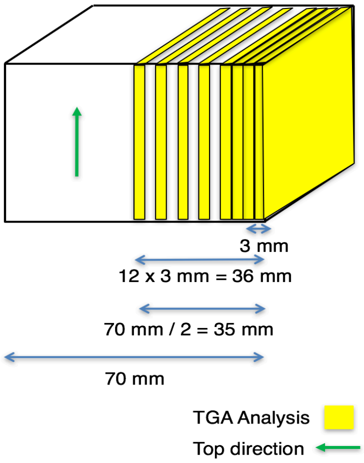

Figure 13, TGA analysis on profile ground sample

The TGA was performed using a Mettler Toledo TGA/DSC 3+ on approximately 300 mg of powder loaded in 600 µl alumina crucibles. During TGA the sample in heated from 40 °C to 900 °C at a rate of 20 °C per minute while the oven is purged with N_2 at 50 ml/min.

The weight loss of the sample is monitored and plotted as a function of temperature. The weight loss due to the release of bound water (H) in the hydrates, decomposition of portlandite (CH), and release of CO_2 is measured in the respective temperature intervals 105–550 °C, 440– 530 °C, and 530–810 °C. (De Weerdt et al., 2014)

Using equations 2-5 the paste content of the powder is calculated. The quantity of aggregate in the concrete in the sample is then calculated as the rest of the sample, see equation 5b.

$$\frac{w_{105} - w_{550}}{w_{810}} = H \qquad [2]$$

With:

- w_{105}, the weight measured at 105 °C in mg

- w_{550}, the weight measured at 550 °C in mg
- w_{810}, the weight measured at 800 °C in mg
- H, the % of hydrate water

$$\frac{w_{440} - w_{530}}{w_{810}} * \frac{M(Ca(OH)_2)}{M(H_2O)} = CH \qquad [3]$$

With:

- w_{440}, the weight measured at 440 °C in mg
- w_{530}, the weight measured at 530 °C in mg
- w_{810}, the weight measured at 810 °C in mg
- $M(Ca(OH)_2)$, the molar mass of calcium hydroxide (portlandite), 74 g/mol
- $M(H_2O)$, the molar mass of water, 18 g/mol
- CH, the % of calcium hydroxide (portlandite)

$$\frac{w_{530} - w_{820}}{w_{810}} = C \qquad [4]$$

With:

- w_{530}, the weight measured at 530 °C in mg
- w_{820}, the weight measured at 820 °C in mg
- w_{810}, the weight measured at 810 °C in mg
- C, the % mass loss due to decomposition of carbonates

$$\frac{w_{440} - w_{530}}{w_{810}} * \frac{1}{5.6\%} = Cem \qquad [5a]$$

With:

- w_{440}, the weight measured at 440 °C in mg
- w_{530}, the weight measured at 530 °C in mg
- w_{810}, the weight measured at 810 °C in mg
- 5.6 %[6], the % weight loss of cement
- Cem, the % of cement in the concrete sample.

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[6] This is the % of weight loss (relative to the dry mass at 810°C) corresponding to portlandite. Klaartje De Weerdt measured an 23 weight% of portlandite in a 100% cement with 87% hydration (2011). I assume the same rate of hydration for my prisms and with that assume the same weight% of portlandite. The weight% of portlandite is then converted to H_2O-weigth loss as this is what I measure, by dividing the molar mass of water to that of portlandite and multiply with this weight% of portlandite, see equation 5d.

$$\frac{M(H_2O)}{M(Ca(OH)_2)} * 23\% = 5.6\% \qquad [5d]$$

With:

- $M(H_2O)$, the molar mass of water, 18 g/mol
- $M(Ca(OH)_2)$, the molar mass of calcium hydroxide (portlandite), 74 g/mol

$$Cem * (1 + w/c) = P \tag{5b}$$

With:

- Cem, the % of cement in the concrete sample from equation 5a.
- w/c, the water/cement-ratio
- P, the paste content in the concrete sample

$$1 - P = A \tag{5c}$$

With:

- P, the % of paste in the concrete sample from equation 5b.
- A, the % of aggregate in the concrete sample

The temperature limits for the different elements of the concrete are decided by analysing the first derivative curve of the weight loss. The levels are the same in all the samples, this is probably because the prism A and W are made with the same concrete.

The TGA results are taken into account when calculating the alkali content of the cement in the concrete by knowing the aggregate content of the sample. By assuming the ratio between fines and coarse aggregate is the same as in the recipe, the quantity of the given aggregate in the concrete is calculated. This is then used in equations 7b and 8 to calculate the alkali content of the cement in the sample, accounting for alkali contribution of the aggregates.

3 Calculations

3.1 Analysis of CWE and HAE solutions

3.1.1 Calculation of free and total alkali content

The ICP-MS-results in µg/L of solution which is converted to mmol / g of powder using equation 6.

$$\frac{[x]_{filtrated\ solution} * D}{M(x)} * \frac{m_{liquid} * 10^{-3}}{m_{powder}} = X \qquad [6]$$

With:

- x, measured element Na or K
- $[x]_{filtrated\ solution}$, the concentration of the element x measured by ICP-MS in µg/L of solution
- D, the dilution factor
- M(x), the molar mass of the element x, 23 g/mol for Na and 39 g/mol for K
- m_{liquid}, the mass of liquid (deionized water during CWE, and acid during HAE) added to the powder in g. Assuming the density of the liquid is 1 g/ml the factor 10^{-3} is included to convert the answer to mmol/kg
- m_{powder}, the mass of sample powder in g
- X, the content of element X in the sample powder, in mmol/kg of powder

Knowing the content of Na and K in mmol / kg of powder, the measured alkali content in the concrete sample is converted to kg Na_2O_{eq} /m^3 concrete using equation 7a.

$$\left(\frac{Na}{2} + \frac{K}{2}\right) * M(Na_2O) * \rho_{CONCRETE} * 10^{-6} = Na_2O_{eq,concrete} \qquad [7a]$$

With:

- Na and K, the amount of Na and K from equation 6
- $M(Na_2O)$, the molar mass of Na_2O, 61.98 g/mol
- $\rho_{CONCRETE}$, the density of the concrete in kg/m^3 from the recipe
- $Na_2O_{eq,concrete}$, the alkali content in the concrete originating from the cement and aggregates in kg Na_2O_{eq} / m^3

The same method is applied for the determination of the alkali contribution from aggregates to CWE and HAE. The density of concrete in equation 7a has to be replaced with the quantity of the given aggregate in kg/m^3 of concrete in equation 7b. This gives the alkali release from the aggregate in kg Na_2O_{eq} / m^3 of concrete. The quantity of aggregtes is known from the recipe or determined with TGA.

$$\left(\frac{Na}{2} + \frac{K}{2}\right) * M(Na_2O) * Q_{Agg} * 10^{-6} = Na_2O_{eq,aggregate} \qquad [7b]$$

With:

- Na and K, the amount of Na and K in the sample powder, in mmol/kg of powder
- $M(Na_2O)$, the molar mass of Na_2O, 61.98 g/mol
- Q_{Agg} , the quantity of the aggregate in kg/m^3 from the recipe or TGA
- $Na_2O_{eq,aggregate}$, alkali content in the concrete originating from the aggregate in kg Na_2O_{eq} / m^3

The amount of kg Na_2O_{eq} / m^3 of concrete in the concrete originating from the cement is calculated using equation 8.

$$Na_2O_{eq,concrete} - Na_2O_{eq,aggregates} = Na_2O_{eq,cem} \qquad [8]$$

With:

- $Na_2O_{eq,concrete}$, alkali content in the concrete originating from the cement and the aggregates in kg Na_2O_{eq} / m^3
- $Na_2O_{eq,aggregates}$, alkali content in the concrete originating from the aggregates in kg Na_2O_{eq} / m^3
- $Na_2O_{eq,cem}$, alkali content originating from the cement in kg Na_2O_{eq} / m^3

This equation assumes that there is no release from aggregates into the pore water during exposure. I repeat that the aggregates tested were “fresh” aggregates that had not been cast in concrete. This may lead to an underestimation of the alkali content in the cement.

3.1.2 Error propagation for free and total alkali content calculations

The determination of free and total alkali from CWE and HAE is prone to both random and systemic error. Because of this I have done error propagation calculations to determine the magnitude of these errors.
The error of CWE- and HAE-calculations is presented in equations 9-12.

The error of equation 6 is given in equation 9.

$$|X|\sqrt{(\frac{\partial[x]_{filtrated\ solution}}{[x]_{filtrated\ solution}})^2 + (\frac{\partial D}{D})^2 + (\frac{\partial m_{powder}}{m_{powder}})^2 + (\frac{\partial m_{liquid}}{m_{liquid}})^2} = \partial X \qquad [9]$$

With:

- x, measured element Na or K
- X, the measured amount of element X in the sample powder in mmol/kg of powder
- $\partial[x]_{filtrated\ solution}$, error for the concentration of element x measured by ICP-MS in µg/L, given in chapter 3.3
- $[x]_{filtrated\ solution}$, concentration of element x measured by ICP-MS in µg/L
- ∂D, error of the dilution factor, given in chapter 3.3
- D, the dilution factor

- ∂m_{powder}, the error of the mass of sample powder in g, given in chapter 3.3
- m_{powder}, the mass of sample powder in g
- ∂m_{liquid}, the error of the mass of liquid (deionized water during CWE, and acid during HAE) added to the powder in g, given in chapter 3.3
- m_{liquid}, the mass of liquid (deionized water during CWE, and acid during HAE) added to the powder in g
- ∂X, error of the measured element concentration in the sample powder in mmol/kg of powder

Equation 7 is decomposed to express only the contribution from alkalis. This is given in equation 10a, and the associated error in equation 10b.

$$\left(\frac{Na}{2}+\frac{K}{2}\right) = A \qquad [10a]$$

With:

- Na and K, the measured element concentration in the sample powder in mmol/kg of powder
- A, the contribution of the measured alkali to equation 7 in mmol/kg of powder

$$\frac{1}{2} * \sqrt{\partial Na^2 + \partial K^2} = \partial A \qquad [10b]$$

With:

- ∂Na and ∂K, the error of the measured element concentration in the sample powder in mmol/kg of powder from equation 9.
- ∂A, the error contribution of the measured alkali to equation 3 in mmol/kg of powder

Then the error of the measured alkali content in the concrete sample in equation 7a is given in equation 11a.

$$\left|Na_2O_{eq}\right|\sqrt{(\frac{\partial A}{A})^2 + (\frac{\partial \rho_{CONCRETE}}{\rho_{CONCRETE}})^2} = \partial Na_2O_{eq,concrete} \qquad [11a]$$

With:

- Na_2O_{eq}, alkali content in kg Na_2O_{eq} / m^3
- ∂A, the error contribution of the measured alkali to equation 7 in mmol/kg of powder from equation 10b
- A, the contribution of the measured alkali to equation 7 in mmol/kg of powder from equation 10a
- $\partial \rho_{CONCRETE}$, the error of the density of concrete in kg/m^3 given in chapter 3.3
- $\rho_{CONCRETE}$, the density of concrete in kg/m^3 from the recipe
- ∂Na_2O_{eq}, error of the alkali content in kg Na_2O_{eq} / m^3

And the error of measured alkali content in the aggregate sample in equation 7b is given in equation 11b.

$$|Na_2O_{eq}|\sqrt{(\frac{\partial A}{A})^2 + (\frac{\partial Q_{Agg}}{Q_{Agg}})^2} = \partial Na_2O_{eq,aggregate} \qquad [11b]$$

With:

- Na_2O_{eq}, alkali content in kg Na_2O_{eq} / m^3
- ∂A, the error contribution of the measured alkali to equation 7 in mmol/kg of powder from equation 10b
- A, the contribution of the measured alkali to equation 7 in mmol/kg of powder from equation 10a
- ∂Q_{Agg} , the error of the quantity of aggregate in kg/m^3 of concrete given in chapter 3.3
- Q_{Agg} , the quantity of aggregate in kg/m^3 of concrete from the recipe or TGA result
- ∂Na_2O_{eq}, error of the alkali content in kg Na_2O_{eq} / m^3

The error for the total amount of alkali in the cement in equation 8 is given in equation 12.

$$\sqrt{\partial Na_2O_{eq,concrete}{}^2 + \partial Na_2O_{eq,aggregate}{}^2} = \partial Na_2O_{eq,cem} \qquad [12]$$

With:

- $\partial Na_2O_{eq,concrete}$, the error of the alkali content in the concrete in kg Na_2O_{eq} / m^3 calculated from 11a
- $\partial Na_2O_{eq,aggregate}$, the error of the alkali content in the aggregates in kg Na_2O_{eq} / m^3 from equation 11b
- $\partial Na_2O_{eq,cem}$, the error of the alkali content in the cement in kg Na_2O_{eq} / m^3

3.2 Performance test measurement analysis

In Lindgård's PhD and for COIN WP2 the alkali content was not measured by CWE or HAE, but by analysing the water, lining and wrapping (if present) in the performance test containers.

For prism S and A, the alkali in the water in the bottom of the container was measured at the measurement intervals given in table 1. This was done to show how the alkali leached out over time. However, for prism A, the last measurement is the more correct as this also account for the lining. The lining was submerged in deionized water for a week until an alkali equilibrium was reached. The water in which the lining was submerged was then analysed for Na and K by flame spectroscopy.

For prism W, only one measurement was performed at the end of the exposure period. This is because, in order to measure ingress, the alkali in the lining and wrapping has to be tested by submerging them in deionized water, and this is only possible to do after the exposure period.

Prism E was sealed in epoxy and thus no leaching was determined..

3.2.1 General performance test leaching calculations

For all the measurements, a 20 ml sample of the water was extracted at the given intervals (see Table 1) and sent to analysis. The water was collected either from the bottom of the test container, or from the supplementary containers where the lining and wrapping was submerged for a week after the exposure period was over, see Table 5.

Table 5, Water sample origins for each prism

Prism	Water sample extracted from
S	– The water in the bottom of the test container
A	– The water in the bottom of the test container – The water in the supplementary container where the lining was submerged after the exposure period
W	– The water in the bottom of the test container – The water in the supplementary container where the lining was submerged after the exposure period – The water in the supplementary container where the wrapping was submerged after the exposure period

The samples were analysed by flame spectroscopy. The measurement yielded a concentration of Na and K in mg/l solution. This was converted to an concentration of mg Na_2O_{eq} /L using equation 13.

$$\left(\frac{Na\left[\frac{mg}{L}\right]}{2*M(Na)}+\frac{K\left[\frac{mg}{L}\right]}{2*M(K)}\right) * M(Na_2O_{eq}) = Na_2O_{eq,sample} \qquad [13]$$

With:

- Na or K, flame spectroscopy measured concentration of element in mg/L
- $M(Na)$, the molar mass of Na, 23 g/mol
- $M(K)$ the molar mass of K, 39 g/mol
- Na_2O_{eq}, alkali content in mg Na_2O_{eq} / L of sample water

The total amount of alkali in the water in the container was then calculated by multiplying the concentration in the sample by the water volume in the container. The water volume was measured by weighing the container. The leached alkali is then calculated as g Na_2O_{eq} using equation 14.

$$Na_2O_{eq,sample} * V_{water} * 10^{-3} = Na_2O_{eq,water} \qquad [14]$$

With:

- $Na_2O_{eq,sample}$, the measured amount of mg Na_2O_{eq} /L in the water sample from equation 13
- V_{prism}, the volume of water in the container in L
- $Na_2O_{eq,water}$, the total amount of g Na_2O_{eq} in the water

The total amount of g Na_2O_{eq} in the container is given by equation 15. This is the sum of calculated g Na_2O_{eq} in the water in the bottom of the container, the water in which the lining was submerged after the exposure period and the water in which the wrapping was submerged after the exposure period.

$$Na_2O_{eq,water,BOC} + Na_2O_{eq,water,lin} + Na_2O_{eq,water,wrap} = Na_2O_{eq,tot} \qquad [15]$$

With:

- $Na_2O_{eq,water,BOC}$, the total amount of g Na_2O_{eq} in the water in the bottom of the container
- $Na_2O_{eq,water,lin}$, the total amount of g Na_2O_{eq} in the water in which the lining was submerged after the exposure period
- $Na_2O_{eq,water,wrap}$, the total amount of g Na_2O_{eq} in the water in which the wrapping was submerged after the exposure period
- $Na_2O_{eq,tot}$, the total amount of g Na_2O_{eq} in the container

To calculate leaching, the original alkali content in the prisms must be calculated from the concrete recipe. This is done using equation 16.

$$\%Na_2O_{eq,cement} * Q_{cement} * V_{prism} * n_{prisms} = Na_2O_{eq,prisms,0} \qquad [16]$$

With:

- $\%Na_2O_{eq,cement}$, the alkali content of the cement
- Q, the quantity of cement in kg/m^3 of concrete
- V_{prism}, the volume of one prism in m^3
- n_{prisms}, the number of prisms in one container
- $Na_2O_{eq,prisms,0}$, the total original amount of g Na_2O_{eq} in the prisms

The leaching of alkali is calculated as a percentage by dividing the measured alkali in the water by the total original alkali in the prisms using equation 17.

$$\frac{Na_2O_{eq,tot}}{Na_2O_{eq,prisms,0}} = R \qquad [17]$$

With:

- $Na_2O_{eq,tot}$, the total amount of g Na_2O_{eq} in the container from equation 15
- $Na_2O_{eq,prisms,0}$, the total original amount of g Na_2O_{eq} in the prisms from equation 16

- R, the reduction of alkali content in the prisms

3.2.1.1 Leaching calculation of Prism S

For prism S the water was replaced at every measuring interval, so the total leached alkali is calculated by adding up the reduction in alkali content from each reading using equation 18.

$$R = \sum_{i=0}^{n} R_i \tag{18}$$

With:

- R, the reduction of alkali in the prisms at the end of exposure period
- R, the reduction of alkali in the prisms after measurement i from equation 17

3.2.1.2 Leaching calculation of Prism A

For prism A the total amount of alkali in the bottom of the container is calculated after the last measurement using equation 19. As the water was not replaced after each measurement, the alkali extracted during the previous measurements is accounted for by multiplying the measured alkali content with the measurement size of 20 ml.

$$\begin{aligned} &\sum_{i=0}^{n-1}\left(Na_2O_{eq,sample,i} * 20\,ml * 10^{-3}\right) + \\ &\left(Na_2O_{eq,sample,n} * V_{water} * 10^{-3}\right) = Na_2O_{eq,water,BOC} \end{aligned} \tag{19}$$

With:

- $Na_2O_{eq,sample,i}$, the known amount of mg/L Na_2O_{eq} in the water from the measurement i
- $Na_2O_{eq,sample,n}$, the known amount of mg/L Na_2O_{eq} in the water from the measurement n
- V_{water}, the known volume of water in the container at measurement n in ml
- $Na_2O_{eq,water,BOC}$, the total amount of g $Na_2O_{eq,n}$ in the water in the bottom of the container at measurement n

Prism A also has a lining in the container. The alkali from the lining is calculated using equations 13 and 14. The total leached alkali is calculated using equation 15 with the value for $Na_2O_{eq,water,BOC}$ from equation 19. The reduction in alkali content is calculated using equation 17.

3.2.1.3 Ingress calculation of Prism W

For prism W the alkali solution in the wrapping was suspected to cause ingress of alkali in the prism. Therefore, the calculation procedure is based on the principle that if there is less alkali in the container after the exposure period, than it was in the alkali solution at the start of the exposure, the alkali from the solution must have gone into the prism.

For prism W, the change in alkali content is calculated after the exposure period by testing the water in the bottom of the container, the wrapping and the lining. The alkali content in these are calculated using equations 13 and 14.

Because this sample is expected to have experienced alkali ingress, this is calculated by calculating the amount of g Na_2O_{eq} in the wrapping at the beginning of the exposure using equation 20, and subtracting the sum of all the alkali in the container water, lining and wrapping at the end of the exposure using equation 21 and finally dividing by the original alkali content using equation 22.

The calculation of the alkali content at the start of the exposure is done by calculating the amount of g Na_2O_{eq} in the wrapping. The wrapping was soaked in an alkaline solution with pH 14.2. The solution contained 19 g NaOH /L and 53 g KOH / L. On average, one wrapping would hold 0,062 L of solution. This was tested in Lindgård's PhD. The alkali content in the in g Na_2O_{eq} was then calculated by knowing the molar mass of the elements in and the composition of the solution, using equation 20.

$$\left(\frac{NaOH}{2*M(NaOH)}+\frac{KOH}{2*M(KOH)}\right)*M\left(Na_2O_{eq}\right)*V_{wrap} = Na_2O_{eq,wrap,0} \qquad [20]$$

With:

- NaOH, the concentration of NaOH in the solution in g/L
- M(NaOH), the molar mass of NaOH, 40 g/mol
- KOH, the concentration of KOH in the solution in g/L
- M(KOH), the molar mass of KOH, 56.19 g/mol
- $M(Na_2O_{eq})$, the molar mass of Na_2O_{eq} in g/mol
- V_{wrap}, the amount of solution the wrapping could hold on average in L
- $Na_2O_{eq,wrap,0}$, the total amount of g Na_2O_{eq} in the wrapping before exposure

The total amount of alkali that has gone from the wrapping into the prism is calculated using equation 21.

$$\begin{aligned} &Na_2O_{eq,wrap,0} - Na_2O_{eq,water,wrap} - \\ &Na_2O_{eq,water,lin} - Na_2O_{eq,water,BOC} = Na_2O_{eq,tot} \end{aligned} \qquad [21]$$

With:

- $Na_2O_{eq,wrapping,0}$, the total amount of g Na_2O_{eq} in the wrapping before exposure from equation 20
- $Na_2O_{eq,water,BOC}$, the total amount of g Na_2O_{eq} in the water in the bottom of the container calculated using equations 13 and 14
- $Na_2O_{eq,water,lin}$, the total amount of g Na_2O_{eq} in the water that the lining was submerged in after the exposure period calculated using equations 13 and 14
- $Na_2O_{eq,water,wrap}$, the total amount of g Na_2O_{eq} in the water that the wrapping was submerged in after the exposure period calculated using equations 13 and 14

- $Na_2O_{eq,tot,ingress}$, the total amount of g Na_2O_{eq} that has gone out of the wrapping and into the prism

The ingress I is then calculated as the amount of alkali in the prism after the exposure period divided by the original alkali content of the prism.

$$\frac{Na_2O_{eq,tot,ingress}}{Na_2O_{eq\ 0,prism}} = I \qquad [22]$$

With:

- $Na_2O_{eq,tot,ingress}$, the total amount of g Na_2O_{eq} that has gone out of the wrapping and into the prism from equation 21
- $Na_2O_{eq\ 0,prisms}$, the total original amount of g Na_2O_{eq} in the prism from equation 16
- I, the % of ingress of alkali in the prism after exposure

3.2.2 Error propagation of performance test leaching measurements

As the calculations for alkali leaching are dependent on many variables there is an error to the calculations. This error can be assessed by doing error propagation calculations. I assume that all errors are uncorrelated.

For the general equations for alkali leaching measurements given in equations 13-15, the errors are given from equations 25-30.

Equation 13 is decomposed to express only the contribution from the alkali measurements in equation 23-24, with error in equation 25–27.

$$\left(\frac{Na}{2 * M(Na)}\right) * M(Na_2O) = Na_2O_{eq,Na} \qquad [23a]$$

With:

- Na, flame spectroscopy measured concentration of Na in mg/L
- $M(Na)$, the molar mass of Na, 23 g/mol
- $M(Na_2O)$, the molar mass of $Na_2O_{eq,}$ 61.98 g/mol
- $Na_2O_{eq,Na}$, the contribution to the total Na_2O_{eq} in the sample from Na

$$\left(\frac{K}{2 * M(K)}\right) * M(Na_2O) = Na_2O_{eq,K} \qquad [23b]$$

With:

- K, flame spectroscopy measured concentration of K in mg/L
- $M(K)$, the molar mass of K, 23 g/mol
- $M(Na_2O)$, the molar mass of $Na_2O_{eq,}$ 61.98 g/mol
- $Na_2O_{eq,K}$, the contribution to the total Na_2O_{eq} in the sample from K

The total Na_2O_{eq} for the sample is then calculated as the sum of equation 23a and 23b, given in equation 24.

$$Na_2O_{eq,Na} + Na_2O_{eq,K} = Na_2O_{eq,sample} \qquad [24]$$

With:

- $Na_2O_{eq,Na}$, the contribution to the total Na_2O_{eq} in the sample from Na from equation 23a
- $Na_2O_{eq,K}$, the contribution to the total Na_2O_{eq} in the sample from K from equation 23b
- $Na_2O_{eq,sample}$, the alkali content in mg Na_2O_{eq} / L of sample water

The error of the alkali contribution to equation 13 is given in equations 25a and 25b

$$\left(\frac{\partial Na}{2 * M(Na)}\right) * M(Na_2O) = \partial Na_2O_{eq,Na} \qquad [25a]$$

With:

- ∂Na, the error of the flame spectroscopy measured concentration of Na in mg/L given in chapter 3.3
- $M(Na)$, the molar mass of Na, 23 g/mol
- $M(Na_2O)$, the molar mass of Na_2O, 61.98 g/mol
- $Na_2O_{eq,Na}$, the error of the contribution to the total Na_2O_{eq} in the sample from Na

$$\left(\frac{\partial K}{2 * M(K)}\right) * M(Na_2O) = \partial Na_2O_{eq,K} \qquad [25b]$$

With:

- ∂K, the error of the flame spectroscopy measured concentration of K in mg/L given in chapter 3.3
- $M(K)$, the molar mass of K, 39 g/mol
- $M(Na_2O)$, the molar mass of Na_2O, 61.98 g/mol
- $\partial Na_2O_{eq,K}$, the error of the contribution to the total Na_2O_{eq} in the sample from K

The error of the total Na_2O_{eq} in the sample is given in equation 26.

$$\sqrt{\partial Na_2O_{eq,Na}{}^2 + \partial Na_2O_{eq,K}{}^2} = \partial Na_2O_{eq,sample} \qquad [26]$$

With:

- $\partial Na_2O_{eq,Na}$ and $\partial Na_2O_{eq,K}$, the error of the alkali contribution to equation 13 of element in mg/L
- $\partial Na_2O_{eq,sample}$, the error of the total Na_2O_{eq} in the sample

The error for equation 14, the amount of alkali in the water, is given in equation 27.

$$Na_2O_{eq,water}\sqrt{\left(\frac{\partial Na_2O_{eq,sample}}{Na_2O_{eq,sample}}\right)^2+\left(\frac{\partial V_{water}}{V_{water}}\right)^2}=\partial Na_2O_{eq,water} \qquad [27]$$

With:

- $Na_2O_{eq,water}$, the amount of mg Na_2O_{eq} /L in the water sample from equation 14
- $\partial Na_2O_{eq,sample}$, the error of mg Na_2O_{eq} /L in the sample from equation 26
- $Na_2O_{eq,sample}$, the error of mg Na_2O_{eq} /L in the sample from equation 24
- ∂V_{water}, the error of the volume of water in the container in L, given in chapter 3.3
- V_{water}, the volume of water in the container in L
- $\partial Na_2O_{eq,water}$, the error of mg Na_2O_{eq} /L in the water

The error for equation 15, the total amount of alkali in the container, is calculated in equation 28.

$$\sqrt{\begin{array}{c}\partial Na_2O_{eq,water,BOC}{}^2+\partial Na_2O_{eq,water,lin}{}^2\\+\partial Na_2O_{eq,water,wrap}{}^2\end{array}}=\partial Na_2O_{eq,tot} \qquad [28]$$

With:

- $\partial Na_2O_{eq,water,BOC}$, the error of the total amount of g Na_2O_{eq} in the water in the bottom of the container from equation 27
- $\partial Na_2O_{eq,water,lin}$, the error of the total amount of g Na_2O_{eq} in the water in the container where the lining was submerged after the exposure period from equation 27
- $\partial Na_2O_{eq,water,wrap}$, , the error of the total amount of g Na_2O_{eq} in the water the water in the container where the wrapping was submerged after the exposure period from equation 27
- $\partial Na_2O_{eq,tot}$, the error of the total amount of g Na_2O_{eq} in the container

The error for equation 16, the original alkali content of the concrete prism, is given in equation 29.

$$\left|Na_2O_{eq,prism,0}\right|\sqrt{\begin{array}{c}\left(\frac{\partial \%Na_2O_{eq,cement}}{\%Na_2O_{eq,cement}}\right)^2+\\\left(\frac{\partial Q_{cement}}{Q_{cement}}\right)^2+\left(\frac{\partial V_{prism}}{V_{prism}}\right)^2\end{array}}=\partial Na_2O_{eq,prism,0} \qquad [29]$$

With:

- $Na_2O_{eq,prisms,0}$, the total original amount of g Na_2O_{eq} in the prism(s) from equation 11

- $\partial\%Na_2O_{eq,concrete}$, the error of the known percentage of Na_2O_{eq} in the cement from the recipe given in chapter 3.3
- $\%Na_2O_{eq,cement}$, the known percentage of Na_2O_{eq} in the cement from the recipe.
- ∂Q_{cement}, the error of the quantity of cement in kg/m^3 concrete given in chapter 3.3
- Q_{cement}, the quantity of cement in kg/m^3 concrete from the recipe
- ∂V_{prism}, the error of the volume of the prism(s) in m^3
- V_{prism}, the volume of the prism(s) in m^3
- $\partial Na_2O_{eq,prisms,0}$, the error of the total original amount of g Na_2O_{eq} in the prism(s)

The error for equation 17, the reduction of alkali, is calculated in equation 30.

$$|R|\sqrt{\left(\frac{\partial Na_2O_{eq,tot}}{Na_2O_{eq,tot}}\right)^2+\left(\frac{\partial Na_2O_{eq,prisms,0}}{Na_2O_{eq,prisms,0}}\right)^2} = \partial R \qquad [30]$$

With:

- R, the reduction in alkali content from equation 17
- $\partial Na_2O_{eq,tot}$, the error of the total amount of g Na_2O_{eq} in the container from equation 28
- $Na_2O_{eq,tot}$, the total amount of g Na_2O_{eq} in the container from equation 15
- $\partial Na_2O_{eq,,prism,0}$, error of the total original amount of g Na_2O_{eq} in the prism(s) from equation 29
- $Na_2O_{eq,prism,0}$, the total original amount of g Na_2O_{eq} in the prism(s) from equation 16
- ∂R, the error of the reduction in alkali content

3.2.2.1 Prism S

As the reduction is cumulative due to the water being exchanged after each reading (equation 17), the error too is cumulative and the total error of reduction is given using equation 31.

$$\sqrt{\sum_{i=0}^{n} \partial R_i^{\,2}} = \partial R \qquad [31]$$

With:

- ∂R, the error of the reduction in alkali content after measurement i from equation 30
- ∂R, the error of the reduction in alkali content after exposure period

3.2.2.2 Prism A

The error for the reduction is given using equation 30.

3.2.2.3 Prism W

The error of equation 21 for the total amount of alkali gone from the wrapping into the prism is given in equation 32.

$$\sqrt{\begin{gathered}\partial Na_2O_{eq,wrapping,0}{}^2 + \partial Na_2O_{eq,water,BOC}{}^2 + \\ \partial Na_2O_{eq,water,lin}{}^2 + \partial Na_2O_{eq,water,wrap}{}^2\end{gathered}} = \partial Na_2O_{eq,tot} \qquad [32]$$

With:

- $\partial Na_2O_{eq,wrapping,0}$, the error of the total amount of g Na_2O_{eq} in the wrapping before exposure given in chapter 3.3
- $\partial Na_2O_{eq,water,BOC}$, the error of the total amount of g Na_2O_{eq} in the water in the bottom of the container from equation 26
- $\partial Na_2O_{eq,water,lin}$, the error of the total amount of g Na_2O_{eq} in the water in which the lining was submerged after the exposure period from equation 26
- $\partial Na_2O_{eq,water,wrap}$, the error of the total amount of g Na_2O_{eq} in the water in which the wrapping was submerged after the exposure period from equation 26
- $\partial Na_2O_{eq,tot}$, the error of the total amount of g Na_2O_{eq} that has gone out of the wrapping and into the prism

The error of equation 22, the ingress of alkali, is given by equation 33.

$$|I|\sqrt{(\frac{\partial Na_2O_{eq,tot}}{Na_2O_{eq,tot}})^2 + (\frac{\partial Na_2O_{eq,prism,0}}{Na_2O_{eq,prism,0}})^2} = \partial I \qquad [33]$$

With:

- I, the ingress of alkali in the prisms after exposure from equation 21
- $\partial Na_2O_{eq,tot}$, error of the total amount of g Na_2O_{eq} in the container from equation 32
- $Na_2O_{eq,tot}$, the total amount of g Na_2O_{eq} in the container from equation 21
- $\partial Na_2O_{eq,prisms,0}$, error of the total original amount of g Na_2O_{eq} in the prisms from equation 29
- $Na_2O_{eq,prisms,0}$, the total original amount of g Na_2O_{eq} in the prisms from equation 16
- ∂I, error of the ingress of alkali in the prisms after exposure

3.3 Errors

Table 6, Errors chosen for the variables in the calculations

	Name in the equations	Value	Error (% of value)
ICP-MS measurement	$\partial[x]_{filtrated\ solution}$	1900–54830 µg/L	4 %
Flame spectroscopy measurement	∂Na and ∂K	32–1800 mg/L	4 %
Mass water/Mass powder	∂m_{powder} and ∂m_{liquid}	10 g	1 %
Density concrete prism S and prism E	$\partial \rho_{CONCRETE}$	2416 kg/m^3	1 %
Density concrete prism A and prism W	$\partial \rho_{CONCRETE}$	2143.5 kg/m^3	1 %
Quantity Årdal fine aggregate	∂Q_{Agg}	698.5 kg/m^3	1 %
Quantity Ottersbo coarse aggregate	∂Q_{Agg}	1045 kg/m^3	1 %
Quantity cement	∂Q_{cement}	400 kg/m^3	1 %
Dilution factor	∂D	10.14 for CWE, 10 and 20 for HAE	1 %
%Na_2O_{eq} in prism E and S	$\partial \%Na_2O_{eq,concrete}$,	0.7 %	1 %
%Na_2O_{eq} in prism A and W	$\partial \%Na_2O_{eq,concrete}$,	0.92 %	1 %
Water measurement	∂V_{water}	1.5 – 8.8 L	2%
Volume of prism S	∂V_{prism}	0.001372 m^3	2%
Volume of prism A and W	∂V_{prism}	0.00141 m^3	2%
Error of alkali in wrapping on prism W before exposure	$\partial Na_2O_{eq,wrapping,0}$	2.7 g	50%

The errors are given as a percentage of the measured value. Thus, the bigger value the bigger error. This should not be a problem as most of the values are either constant, or not varying significantly for each calculated error.

The error of the ICP-MS is based on measurements made by Gilles Plusquellec at NTNU. He found a variation of 4% in repeated measurements. The same deviation is used for flame spectroscopy measurements.

The mass of the powder and water is given a 1% error. The balance has a 0.001 g accuracy, but I also account for potential human error.

The density for the concretes and quantities of aggregate and cement is given a 1% error. This is based on the fact that the ingredients are weight on a balance, and I give them all the same error of 1% of the value for potential systemic and human error.

The dilution factor is given a 1% error as the dilution is done by measuring exact quantities of liquids with a pipette which inherits a potential systemic error, and the accuracy is prone to human error.

The volume of the prisms is given a 2% error for the variation of the steel moulds the concrete is cast in, any thermal expansion of these, and the filling of concrete in the mould.

The volume of water is given a 2% error as this is based on weighing the water. I account for a systemic error in the balance, and a potential variance in the mass caused by water left in the container when the water was poured into a new container for weighing.

The error of alkali in wrapping before exposure on prism W is based on the fact that the calculation, given in equation 19, has only one big error source; the volume of solution the wrapping can hold. In the ingress measurements, the figure used is 0.062 L, as this was the what the average wrapping contained in a pilot study of the method made in Jan Lindgård PhD. However, notes from the lab give that the wrapping weight between 111 and 117 g after the exposure period, and the wrapping itself weighs 23 g. Assuming the density of the solution is approximately 1000 g/L, the actual volume of solution in the wrapping could be as much as 0,094 L. With an error of 50%, the maximum volume is 0.093 L.

4 Results

In this chapter the results from TGA, CWE and HAE will be presented. The results will be presented with and without the aggregate quantity found with TGA.

4.1 TGA

In Figure 14–Figure 19 the paste content is presented for the bulk sample in prism E and S, and the length and middle profile in prism A and W. The TGA-evaluations these calculated paste content results are based on are presented in the Appendix. For most of the measured samples the paste content is slightly lower than the paste content given in the recipe. The paste content from the recipe is the nominal paste content based on cement and water weight%. This can be due to my assumption of hydration rate of 87%, as described in chapter 2.2.8.

In Figure 14 and Figure 15 the paste content in prisms E and S is presented respectively. In prism E, the paste content is 20%. In prism S the paste content is 17%. For both prisms, the paste content is less than the 25% paste content given in the recipe.

For all length profile plots, the middle data point at 140 mm is the average of the measured value from the middle profile.

Figure 16 show that the paste content in the middle profile samples for prism A is varying between 19-30%, with a high point at the surface. Figure 17 show the paste content in the length profile samples from prism A. This is varying less than the middle profile. The variation could be due to the 20 mm deep grounded samples rather than 3 mm deep as described in chapter 2.2. The average paste content from TGA for the length profile samples from prism A (Figure 17) and the average for middle profile samples from prism A (Figure 16) is the same at 16%.

Figure 18 show that the paste content in the middle profile samples from prism W is also varying, there is less variation than in prism A, and still a high point in the surface. Figure 19 show the paste content in the length profile samples from prism W. The average paste content from TGA for the length profile samples from prism W and the average for middle profile samples from prism A are 23% and 21% respectivly.

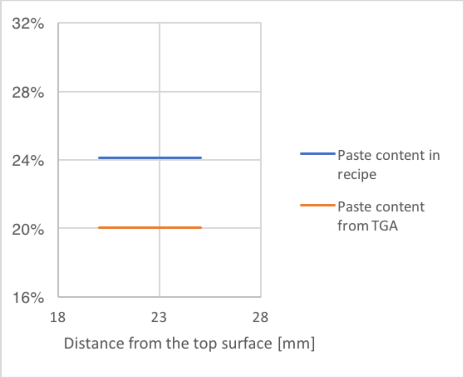

Figure 14, Paste content from TGA in bulk sample, prism E

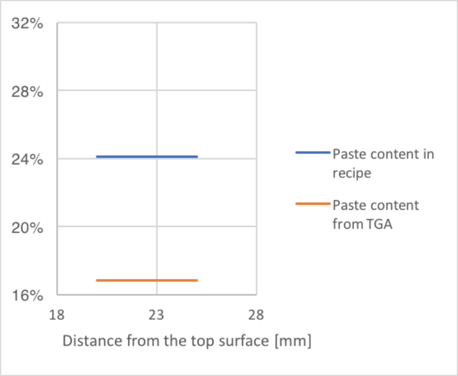

Figure 15, Paste content from TGA bulk sample, prism S

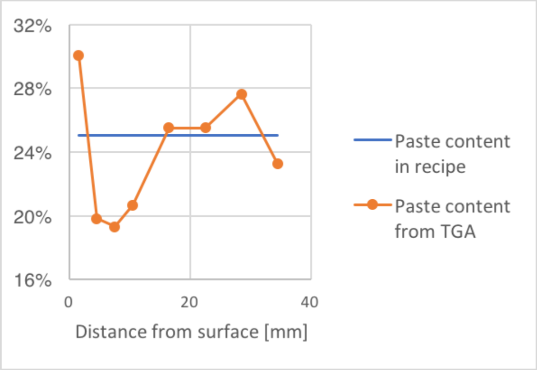

Figure 16, Paste content from TGA in middle profile, prism A

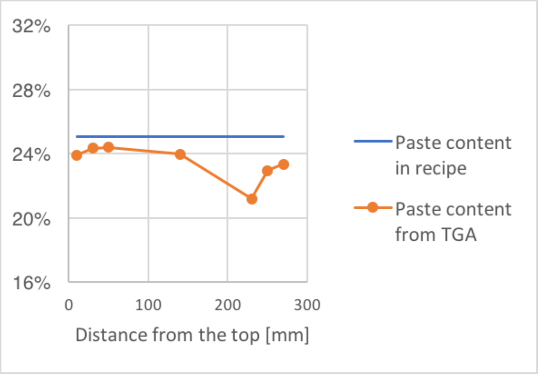

Figure 17, Paste content from TGA in length profile, prism A

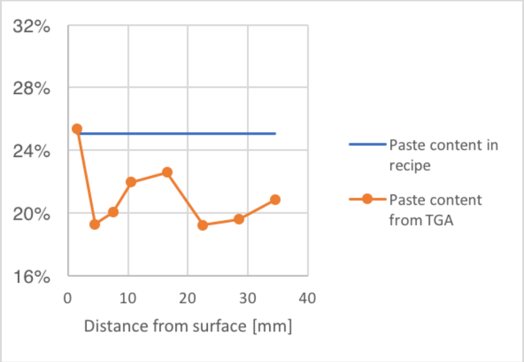

Figure 18, Paste content from TGA in middle profile, prism W

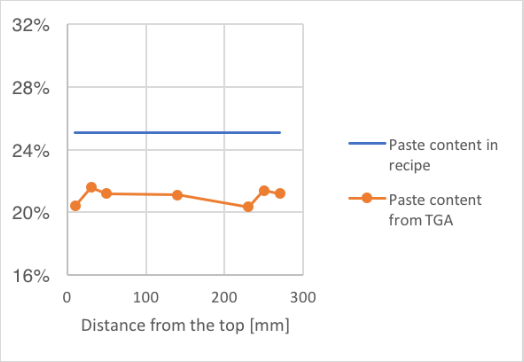

Figure 19, Paste content from TGA in length profile, prism W

In prism E and prism S the TGA measured 1.4 weight% carbonation in the bulk samples.

The measured carbonation from the TGA in prism A and W is presented in Figure 20–Figure 23. This show that prism A is less carbonated than prism W. We see that the samples taken from the surface has more carbonate. The carbonation is low in all samples, and some of the measured carbonation can originate from the cement itself.

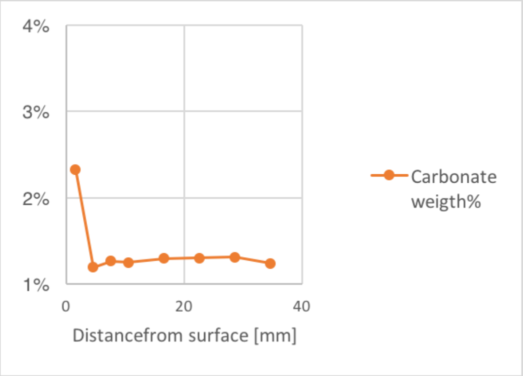

Figure 20, Carbonate weight% from TGA in middle profile, prism A

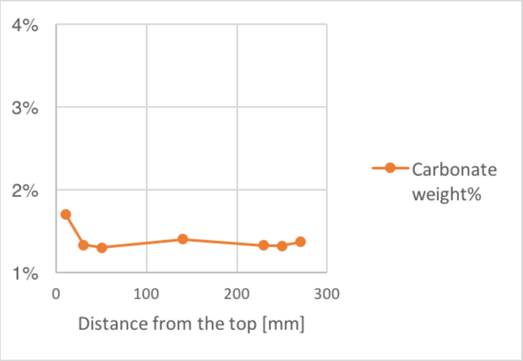

Figure 21, Carbonate weight% from TGA in length profile, prism A

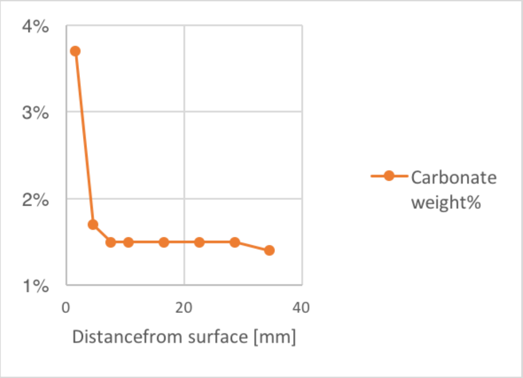

Figure 22, Carbonate weight% from TGA in middle profile, prism W

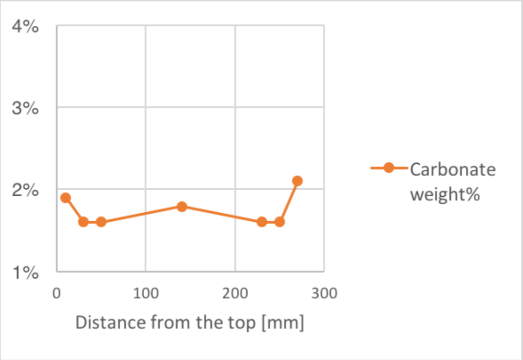

Figure 23, Carbonate weight% from TGA in length profile, prism W

4.2 Bulk measurements

Figure 25–Figure 27 presents the bulk measurement results from the prisms. Table 7 explains the different bars in the figures.

Table 7, Bulk result plot legend explanation

Bar	Info
Recipe	Represents the alkali content given from the recipe. This is calculated using equation 16. This is the alkali in the cement in the concrete when it was cast.
Leachate	Represents the amount of alkali that has left the prism, calculated by multiplying the leaching (or ingress) of alkali from equation 17 (or 22 for ingress) with the original alkali content from equation 16
Recipe – leachate	Represents the expected alkali content in the prism. Calculated by subtracting the second bar from the first bar.
HAE Concrete	Represents the calculated alkali content from the HAE of the bulk concrete powder from equation 7a.
HAE Aggregates	Represents the calculated alkali contribution from the HAE of the aggregates from equation 7b.
HAE Cement w/o TGA	Represents the alkali content from HAE of the concrete minus the contribution from the aggregates measured with HAE and calculated using the quantity of aggregates given in the recipe in equation 7b.
HAE Cement w/ TGA	Represents the alkali content from HAE of the concrete minus the contribution from the aggregates measured with HAE and calculated using the quantity of aggregates measured with TGA in equation 7b.
CWE Concrete	Represents the calculated alkali content from the CWE of the bulk concrete powder from equation 7a.
CWE Aggregates	Represents the calculated alkali contribution from the CWE of the aggregates from equation 7b.
CWE Cement w/o TGA	Represents the alkali content from CWE of the concrete minus the contribution from the aggregates measured with CWE and calculated using the quantity of aggregates given in the recipe in equation 7b.
CWE Cement w/ TGA	Represents the alkali content from CWE of the concrete minus the contribution from the aggregates measured with CWE and calculated using the quantity of aggregates measured with TGA in equation 7b.

The expected alkali in the prism from subtracting the leachate from the recipe, and the measured alkali from HAE and TGA (with and without correcting the quantity of aggregate) for all prisms is plotted in Figure 28.

4.2.1 Prism E

In prism E the alkali content is expected to be exactly what is given in the recipe, therefore this will function as a reference for the CWE and HAE results. The results are presented in figure Figure 24.

When accounting for the aggregate quantity measured with the TGA, HAE yields 0.47 kg Na_2O_{eq} / m^3 with an error of ±0.22 kg Na_2O_{eq} / m3, and CWE yields 0.85 kg Na_2O_{eq} / m^3 with an error of 0.04 kg Na_2O_{eq} / m3. When converting the numbers to percentages of the expected value, HAE measured 12% of the expected 3.68 kg Na_2O_{eq} / m^3 and CWE measured 23%. The error of HAE is more significant than the error of CWE, but for prism E all errors are quite small. The alkali contribution from aggregates is greater from HAE than CWE.

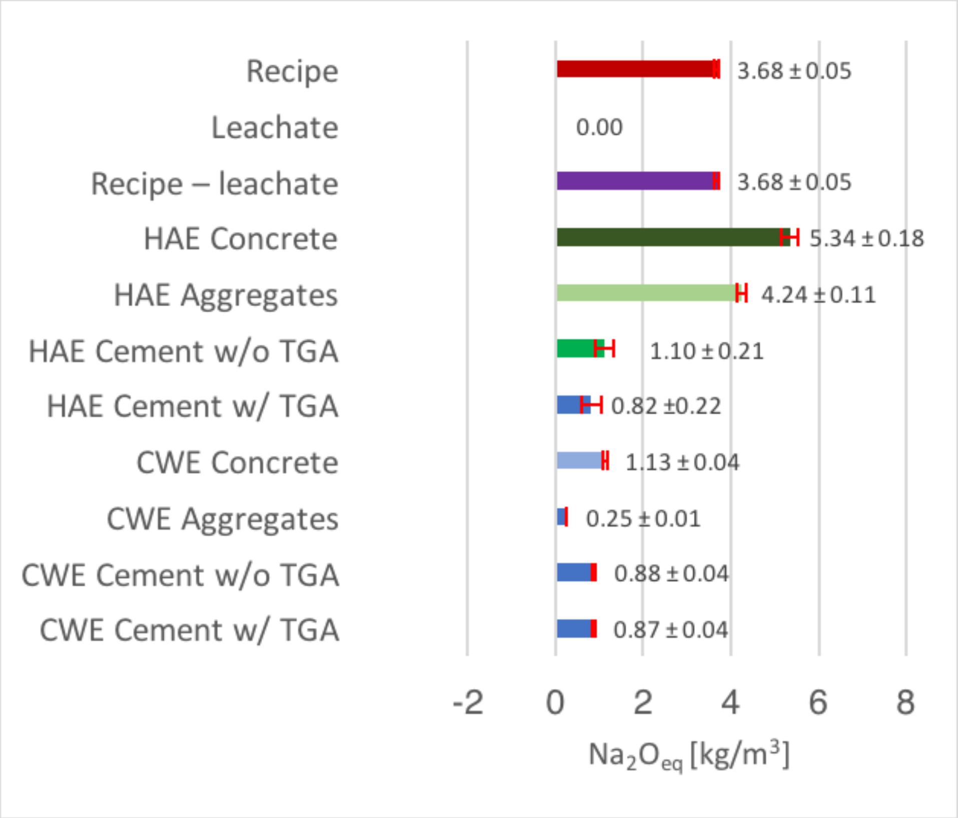

Figure 24, Bulk alkali content and associated error, prism E

4.2.2 Prism S

For prism S the alkali content is expected to be -0.21 kg Na_2O_{eq} / m^3. The error for the expected alkali is 0.28 kg Na_2O_{eq} / m^3 which is more than the expected alkali content itself. The error for the expected alkali content is primarily influenced by the error of the leaching calculation given in equation 30. Lindgård measured 104% leaching, and I have calculated the error of Lindgårds measurements to be ±7%. The results are presented in Figure 25.

When accounting for the aggregate quantity measured with the TGA, HAE yields –0.07 kg Na_2O_{eq} / m^3 with an error of ±0.20 kg Na_2O_{eq} / m^3, and CWE yields 0.29 kg Na_2O_{eq} / m^3 with an error of 0.02 kg Na_2O_{eq} / m^3. Both results are numerically quite close to the expected value, especially considering the error of the expected value. The error for HAE is ten times the error for CWE.

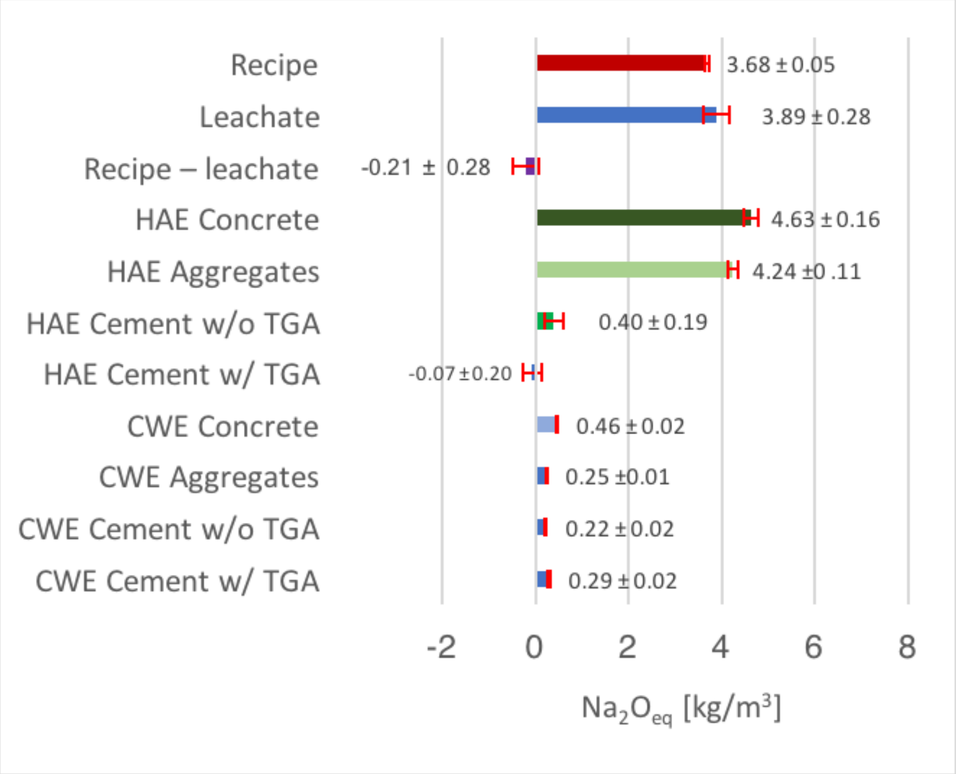

Figure 25, Bulk alkali content and associated error, prism S

4.2.3 Prism A

1.38 kg Na_2O_{eq} / m^3 is expected to be left in prism A according to Lindgård's leaching measurements. The error for the expected alkali content is small at 0.06 kg Na_2O_{eq} / m^3. The results are presented in Figure 26.

HAE without accounting for TGA results gives 1.02 kg Na_2O_{eq} / m^3, but after calculating the quantity of aggregates in the samples from the TGA results the HAE only gives 0.54 kg Na_2O_{eq} / m^3 with. The error for HAE is considerable at 0.21 kg Na_2O_{eq} / m^3 for the HAE measurement with aggregate quantity from the TGA, as this is 39% of the measured alkali.

The CWE results gives 0.56 kg Na_2O_{eq} / m^3, and 0.61 kg Na_2O_{eq} / m^3 when taking TGA results into account. The error for CWE is small at 0.03 kg Na_2O_{eq} / m^3 for both results.

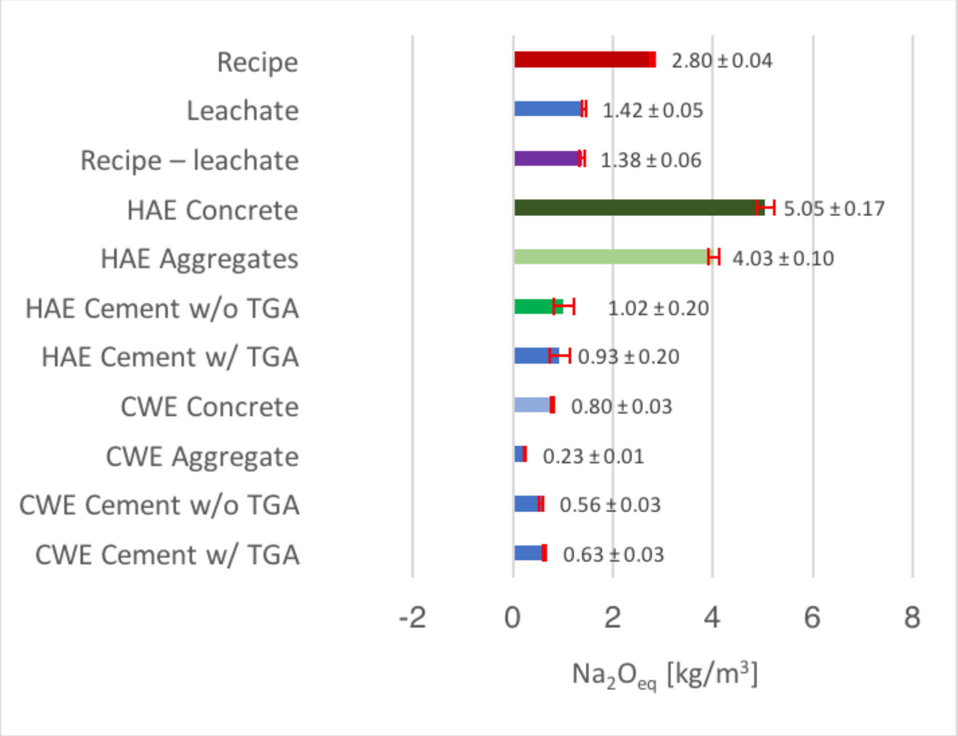

Figure 26, Bulk alkali content and associated error, prism A

4.2.4 Prism W

3.88 kg Na_2O_{eq} / m^3 is expected to be left in Prism W. Lindgård measured that the prism experienced 1.08 kg Na_2O_{eq} / m^3 ingress, but my error calculations show that this may vary from 0.12– 2.04 kg Na_2O_{eq} / m^3. The reason for this important error will be discussed further in chapter 5.1. The results are presented in Figure 27.

HAE without accounting for TGA results gives 2.30 kg Na_2O_{eq} / m^3, but after calculating the quantity of aggregates in the samples from the TGA results the HAE only gives 1.73 kg Na_2O_{eq} / m^3 with. The error for HAE is considerable at 0.25 kg Na_2O_{eq} / m^3 for the HAE measurement with aggregate quantity from the TGA, as this is 14% of the measured alkali.

The CWE results gives 1.48 kg Na_2O_{eq} / m^3, and 1.51 kg Na_2O_{eq} / m^3 when taking TGA results into account. The error for CWE is small at 0.06 kg Na_2O_{eq} / m^3 for both results.

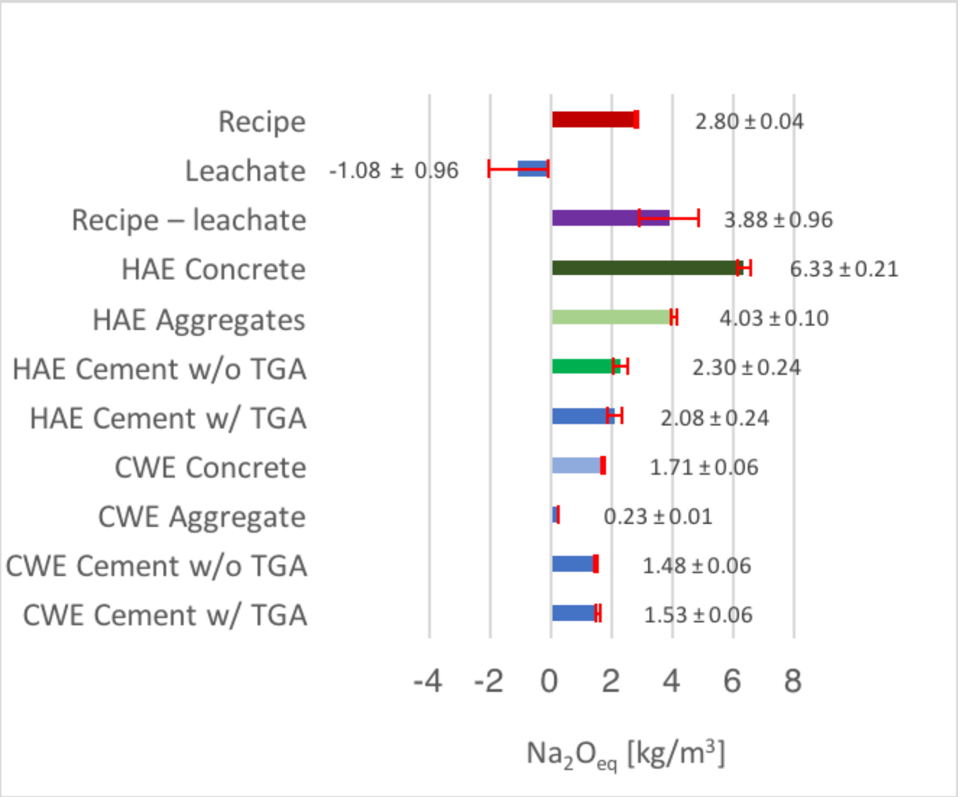

Figure 27, Bulk alkali content and associated error, prism W

4.2.5 Bulk alkali content comparison

The expected alkali content and bulk alkali content from all prisms is presented in Figure 28. The percentages of the expected alkali content measured with each method is given.

HAE varies considerably whether the quantity of aggregates is taken from the recipe or the TGA. CWE is less affected.

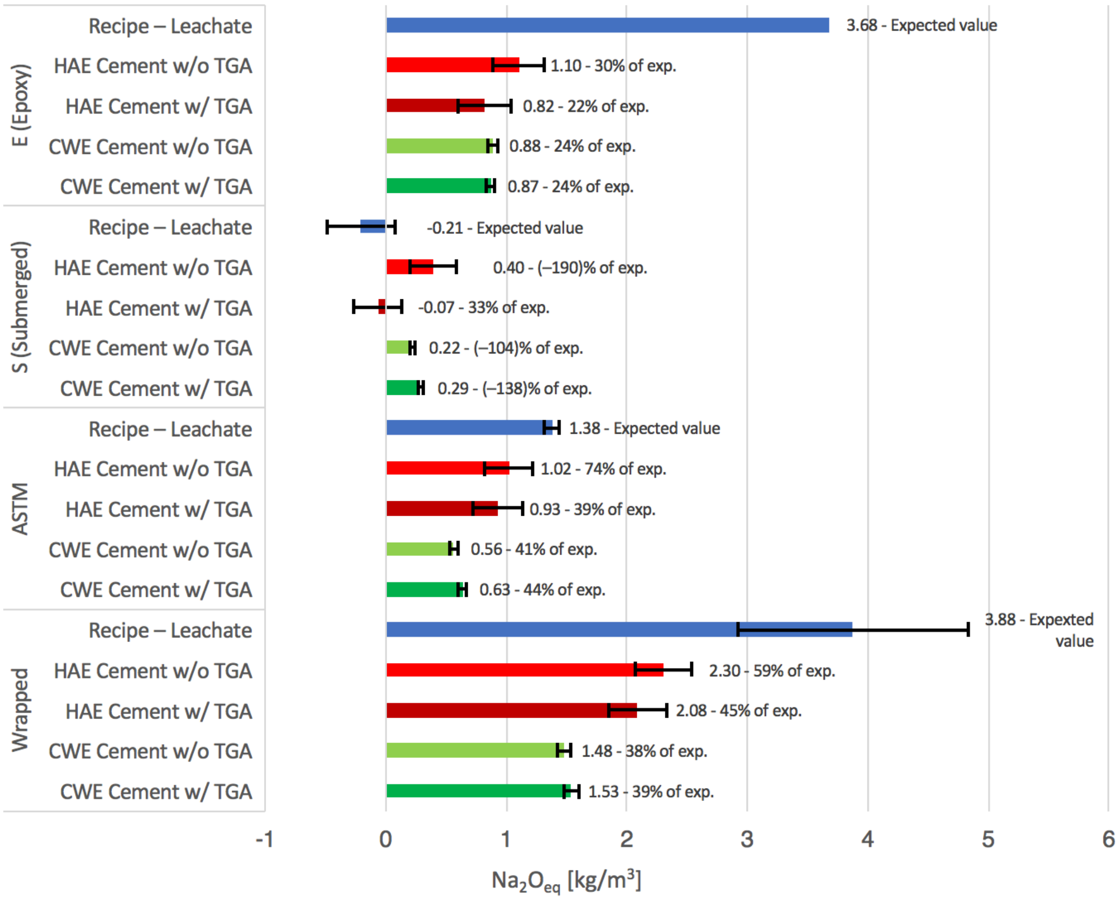

Figure 28, Comparison of bulk alkali content, all prisms

4.3 Profile measurement

4.3.1 Middle alkali profile

4.3.1.1 Prism A

The middle profile alkali content from prism A is plotted in Figure 29 which represents the free alkali content in the function of the distance from the surface. The red line is the CWE results calculated with aggregate quantity from the recipe and the green line is with aggregate quantity determined from the TGA. The difference between the two lines is minimal as the aggregate release measured with CWE is small as per Figure 26.

The measured free alkali in the middle profile fits in between the measured free alkali content in prism S and prism E. This is in accordance with the expectation.

The first sample taken from the surface has a high free alkali content (1.22 kg Na_2O_{eq} / m^3). This is even more than the measured free alkali content from the bulk sample in prism E (0.88 kg Na_2O_{eq} / m^3). The free alkali decreases to approximately 0.3 kg Na_2O_{eq} / m^3 between 5 and 15 mm from the surface, and increases to approximately 0.5 kg Na_2O_{eq} / m^3 between 15 and 40 mm depth.

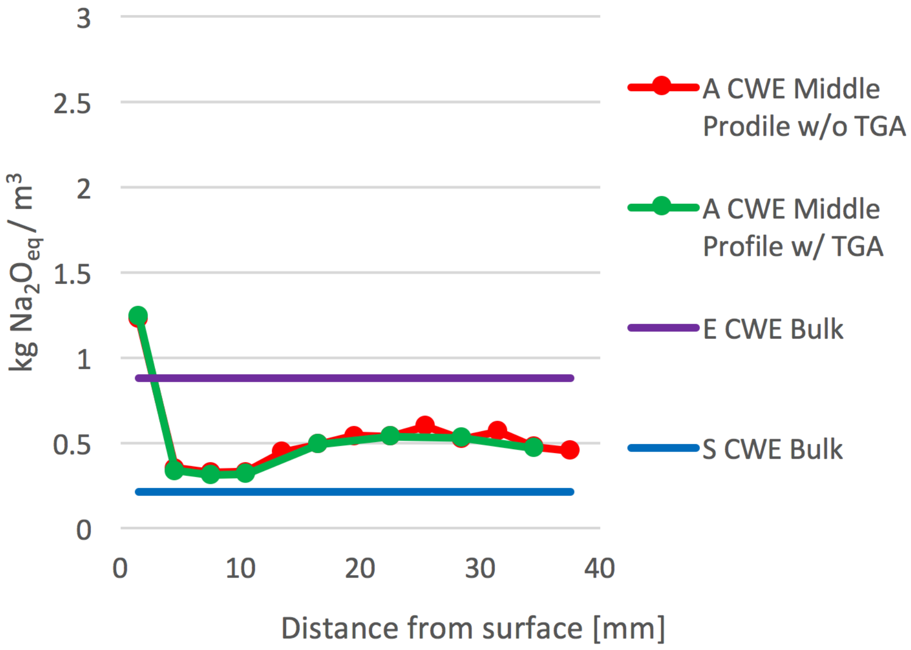

Figure 29, Middle profile alkali content, prism A

4.3.1.2 Prism W

The middle profile alkali content from prism W in Figure 30 is plotted in the same configuration as in Figure 29. The profile is not affected by the aggregate quantity determined from TGA. The free alkali content in the profile samples are all above the bulk free alkali content in prism E, this corresponds with the bulk results presented in Figure 27.

The first sample taken from the surface has a high free alkali content (2.41 kg Na_2O_{eq} / m^3). This is much more than the measured free alkali content from the bulk sample in prism E (0.88 kg Na_2O_{eq} / m^3). The free alkali decreases to approximately 1.2 kg Na_2O_{eq} / m^3 between 5 and 15 mm from the surface, and increases to approximately 1.5 kg Na_2O_{eq} / m^3 between 15 and 40 mm depth.

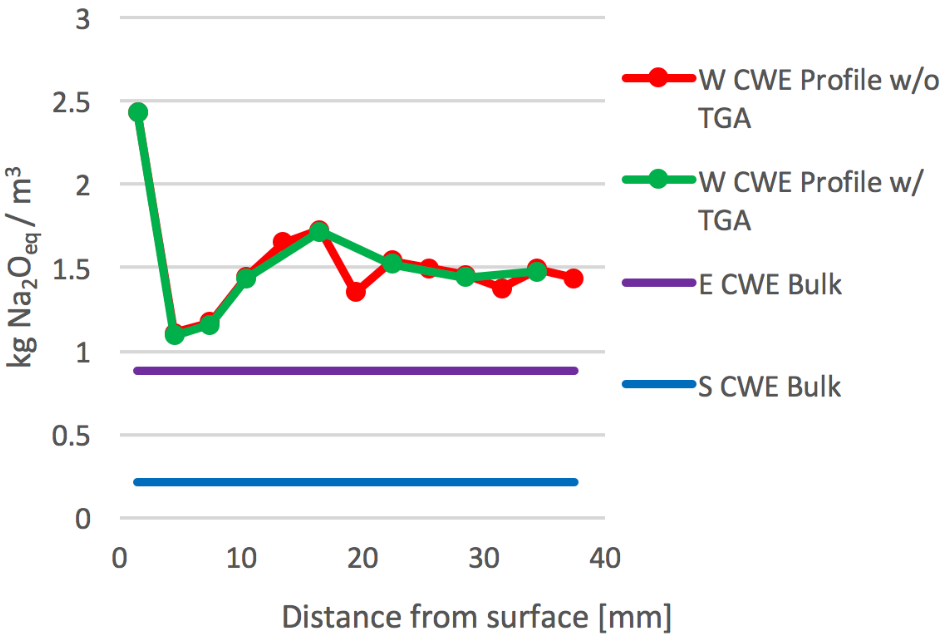

Figure 30, Middle profile alkali content, prism W

4.3.2 Length alkali profile

For all length profile plots, the point in the middle at 140 mm from the topis an average of the measured values from the middle profile

4.3.2.1 Prism A

The length profile for prism A measured with CWE is given in Figure 31. The free alkali content in the top and middle is approximately 0.5 kg Na_2O_{eq} / m^3, and approximately 0.7 kg Na_2O_{eq} / m^3 in the bottom part.

The length profile for prism A measured with HAE is given in Figure 32. More alkali is measured in the bottom than the top, as in the CWE results. However, the variation is significantly greater between the three samples on each side.

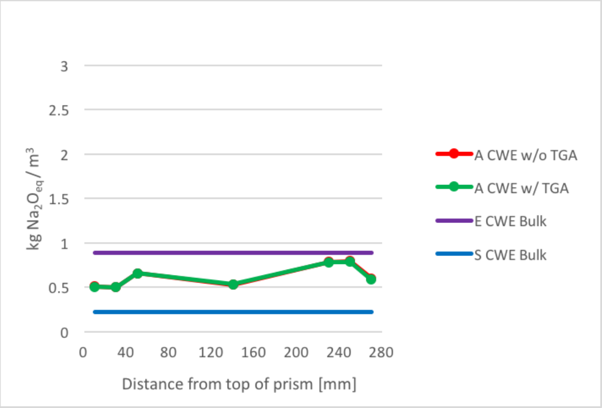

Figure 31, CWE Length profile alkali content, prism A

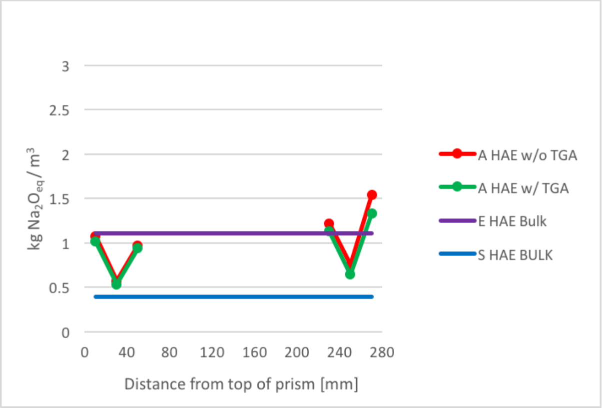

Figure 32, HAE Length profile alkali content, prism A

4.3.2.2 Prism W

The length profile for prism W measured with CWE is given in Figure 33.The free alkali content in the top, middle and the sample taken at 230 mm from the top is approximately 1.5 kg Na_2O_{eq} / m^3, the two last samples in the bottom at 250 mm and 270 mm from the top are approximately 1.1 kg Na_2O_{eq} / m^3.

The length profile for prism A measured with HAE is given in Figure 32. More alkali is measured in the top than the bottom, as in the CWE results. However, the variation is much significantly greater between the three samples on each side.

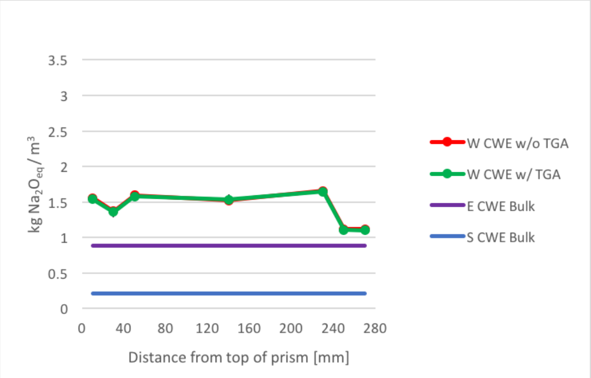

Figure 33, CWE Length profile alkali content, prism W

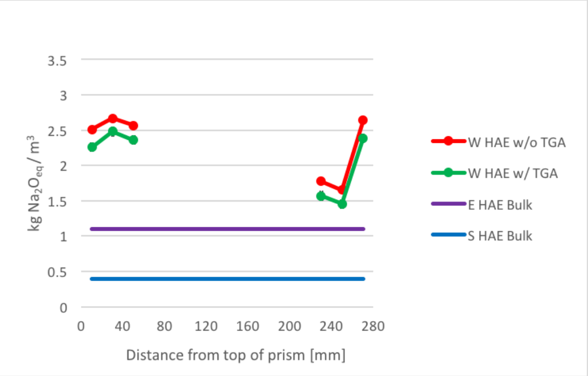

Figure 34, HAE Length profile alkali content, prism W

5 Discussion

5.1 Errors

By doing extensive error calculations on all measurements and calculations the reliability of the results is assessed.

From the leaching measurements done by Jan Lindgård there are two prisms that stand out in the error calculations, prism S and prism W.

As the water was replaced after each measurement of prism S the leaching calculation is cumulative, see equation 18, and therefore the error is also cumulative, see equation 31. This causes the error of the leaching measurement in prism S to be considerable at 7.1% of the measured value. Considering that prism S could have leached out more than all the original alkali content from the cement, this would mean that alkali release from aggregates had to have contributed. However, if the prism leached less than 100%, alkali release from aggregates would not be a certainty, but rather a possibility. Therefore, there is a difference between having leached out 104% as the leaching measurements show, or 98% which is the leaching measurement minus the calculated error, as this is the difference between a proof of release from aggregates and an indication of potential release from aggregates.

The considerable error in Lindgård's leaching measurements for prism S would have been limited if the water had not been changed every time. I would suggest submerging the prism in a larger container with more water to limit the error, while still maximizing alkali leaching.

The ingress calculation of prism W is based on subtracting the alkali found in the container from the calculated original alkali content in the wrapping, see equation 21. The original alkali content in the wrapping is based on the amount of pH 14.2 solution the wrapping can hold, given in equation 20. As discussed in chapter 3.3 this is highly uncertain. Thus, the error of the ingress calculation is 88.9% of the value.

This error could have been avoided if the wrapping was weighed before it was wrapped around the prism, and thus giving a known amount of alkaline solution in the system.

The error of the CWE and HAE measurements are primarily affected by the error of the ICP-MS. As argued in chapter 3.3, this is 4% of the measured value. This means that the more alkali measured with ICP-MS, the bigger error. Because of this, the error for HAE is up to 10 times the error for CWE. However, this way of calculating the error is not necessarily the best way to do it, as it may not be realistic that there is a bigger error when more alkali is measured.

5.2 Sample representativeness

As we can see from Figure 14–Figure 19 the paste content in the samples varies slightly from the paste content given in the recipe. This indicated that TGA provides a good estimation of the paste content in the samples. This is especially important when collecting small samples like I did for the middle profiles where this can potentially vary more, as can be seen in Figure 16 and Figure 18.

It also important to repeat that I assume a hydration rate of 87%, as mentioned in chapter 2.2.8. The assumption of 23% CH given from the assumption of the hydration rate may vary for different cement compositions.

I also assumed the same fine/coarse aggregate ratio as in the nominal recipe, as TGA cannot distinguish between aggregate types. This primarily affects the HAE results as the alkali contribution from aggregates is low during CWE.

5.3 Hot acid extraction (HAE)

HAE is supposed to dissolve all alkali in the concrete and give the total alkali content of the cement when accounting for the aggregate contribution to the concrete. The method may very well do that, but the problem is correcting for the release of alkali from aggregates when calculating the alkali content in the cement using equation 8. Despite accounting for quantity of aggregate from TGA, the correction for the aggregate contribution to HAE is almost the same as the alkali measured in the concrete with HAE, see Figure 25–Figure 27. This could be caused by a more thorough dissolution of the aggregates when only the aggregates themselves were tested, than in the test of a ground concrete sample. Even though the two samples have the same maximum particle size of 80 µm, the distribution of particle sizes smaller than that is not known. I hypothesise that this can be due to the way the samples are ground. As presented in chapter 2.2, aggregates (and concrete samples when necessary) are crushed with a rotary mill. When crushing concrete, the hard aggregates are ground with the softer paste in between. The paste is then ground even finer as it is weaker than the aggregates. The aggregates get ground to a powder too, but potentially not as fine as the paste, because the paste acts as a cushion between the aggregate particles. When grinding the aggregates alone, there is nothing in between, and this could case the aggregates to be crushed finer and produce a finer powder with a larger surface. This could in turn make the aggregates contribute with more alkali during CWE and HAE when analysing aggregates alone than the entire concrete. This should be investigated in follow up studies.

When calculating the quantity of aggregate from the TGA in equation 5c, I assumed that the ratio between the two aggregate types was the same as in the recipe. This assumption is made as it is not possible to differentiate between the two aggregates from the TGA results, but this may give an errorous quantity of a given aggregate type. The two aggregate types contribute with different amounts of alkali, as Årdal fines contribute 2.43 times more alkali than Otterbo coarse when analysed with HAE. It is also important to repeat that the aggregate analysed were fresh aggregate that had never been cast in concrete.

I conclude that HAE is not suitable for measuring total alkali content, and due to HAE high sensitivity to the alkali contribution from aggregates it is hard to assess the validity of the results given with this method.

5.4 Cold water extraction (CWE)

CWE measure the free alkali content, as described in chapter 1.2. The bulk alkali content measured with CWE vary between 24–44% of the expected total alkali for prisms E, A and W, see Figure 28. This is lower than Plusquellec et al. (2017) indicated. This could be caused by external factors, such as the environment in which the samples were stored before cutting and grinding. i.e. the prisms were not packed tightly enough and has suffered carbonation.

The bulk free alkali content measured with CWE in prism A and W is 44% and 39% of the expected alkali content respectively, while only 24% of the expected alkali content is measured in prism E. Prism E was cast in 2008, while prisms A and W were cast in 2011, see Table 3. This could indicate carbonation in the older samples, but as presented in chapter 4.1 the carbonation measured with TGA is similar in all the tested samples. As presented in Figure 20–Figure 23, the measured carbonation in prisms A and W is only considerable in the surface. The relative difference between measured bulk alkali and expected alkali content in prism E and measured bulk alkali content in prisms A and W can be explained by the paste content in the samples given in Figure 14–Figure 19. There we see that the paste content in the bulk samples collected from prisms E and S is slightly lower than in the samples collected from prisms A and W.

CWE results are also calculated taking account for the alkali contribution from aggregates. Again, the fact that the tested aggregates is fresh, and potentially finer ground in the aggregate test sample powder than in the concrete test sample powders, can affect the results as discussed in chapter 5.2. However, the contribution from aggregates is relatively small from CWE compared to HAE, see Figure 25–Figure 27. This in turn makes the measured alkali content from CWE consistent for each prism.

5.5 Leaching and ingress of alkali

When comparing the measured bulk free alkali content in prism A with the measured bulk free alkali content in prism E and S in Figure 28 the free alkali content of prism A is slightly lower than that of prism E and considerably higher than that of prism S. Prism E and S have a higher original alkali content (3.7 kg Na_2O_{eq} / m^3) than prism A and W (2.8 kg Na_2O_{eq} / m^3), so these numbers are not directly comparable. However, the measured bulk free alkali content in prism A and W both yield 38-44% of the expected alkali content, and the measured bulk free alkali content from prism A (0.63 kg Na_2O_{eq} / m^3) is only 42% of the measured bulk free alkali content result of prism W (1.53 kg Na_2O_{eq} / m^3). As I have not tested an epoxy sealed prism with the same original alkali content and same age as prism A to compare with, I can only conclude that leaching is indicated, not proven.

The measured bulk free alkali content for Prism S (0.29 kg Na_2O_{eq} / m^3) is 33% of the measured bulk free alkali content for prism E (0.87 kg Na_2O_{eq} / m^3). This documents that prism S has experienced leaching.

The measured bulk free alkali content results for prism W (1.53 kg Na_2O_{eq} / m^3) documents ingress, as this is 176% of the measured bulk free alkali content for prism E (0.87 kg Na_2O_{eq} / m^3).

5.6 Alkali profiles

As presented in chapter 4.3.1 the measured free alkali content in the middle profiles in prism A and W show a similar trend with higher alkali content in the surface, a decrease below average 5-15 mm from the surface and then a stabilizing from 15-40 mm.

The high free alkali content measured in the surface could be due to paste content. This is supported by the TGA results in Figure 16 for prism A, where the paste content follows a similar trend with more paste in the surface, below average paste content between 5-15 mm from the surface, then a stabilizing from 15-40 mm. As the primary source of alkali to the free alkali content is the paste, it is natural to see a high point in free alkali content corresponding to a high point in paste content. The high point in the paste content measured in the surface can be explained by the wall effect, presented in chapter 2.2.2.3. The low point in paste content between 5-15 mm from the surface can be caused by the wall effect as well, as the aggregates could be accumulating in a bond close to the surface in the mold, see Figure 35. This could happen as the aggregate size of the coarse aggregate is 4–18 mm in both recipes, which is larger than the grinding step, i.e. 3 mm. However, an increase in aggregate content between 5-15 mm from the surface is not clearly indicated in prism W (TGA results in Figure 18). In prism W the paste content between 15-40 mm from the surface is the same as it is between 5-15 mm from the surface. Also, the variation in paste content is not the same as the variation in the free alkali middle profile for prism W.

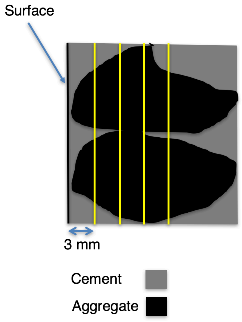

Figure 35, Aggregate accumulation towards the surface

The increase of free alkali towards the surface can also be explained by drying of the surface of the prisms during storage. The prisms are cast in 2011 and have dried during storage. During drying a mechanism called wick action can occur. The pore water is transported towards the surface causing a redistribution of the free alkali ions. Magnus Åhs wrote a PhD in 2011 with the title ‘Redistribution of moisture and ions in cement based materials’. In his PhD Åhs measured the distribution of K^+ ions during drying of a concrete slab. His measurements produced a plot of the K^+ ions distribution in a dried concrete similar to the shape of the curves in Figure 29 and 30. (Åhs, 2011)

Given that the paste content from TGA for prism W do not correspond to the free alkali middle profile, drying of the prisms may be the main cause of the high free alkali content in the surface.

By analyzing the free alkali in the samples 15-40 mm from the surface in the middle profiles for prisms A and W, a slight decrease towards the surface in prism A, and a slight increase towards the surface in prism W, can be observed. This indicates leaching in prism A and ingress in prism W. However, because of the uncertainty of the free alkali content towards the surface in the middle profiles of prism A and W, I cannot conclude that I have sufficient proof for leaching in the part of the prism, and therefore the results are not suitable as visualization of alkali during leaching or ingress. I therefore deem the obtained results from the middle profiles as not conclusive evidence, because of possible redistribution of alkali caused by drying and old age.

The free alkali content measured in the length profiles from prisms A and W should therefore be considered unreliable, as the prisms potentially are dried, and alkali redistributed. However, as the size of the samples taken from the top and bottom is bigger (20 mm thick vs. 3 mm thick), the effect of drying might be limited.

The free alkali content measured in the length profiles from prism A is given in Figure 31. The measured free alkali content profile show more free alkali in the bottom part than the top part of the prism. This can be explained by drops of condensed water that run down the prism and carry alkali from the top to the bottom. The ASTM test method states that the prisms should be turned at every measurement, but Lindgård did not do this in order to investigate if there was a difference in alkali content in the top and bottom. The free alkali content in the top part is close to the average free alkali content measured in the middle profile, but slightly lower towards the surface, indicating leaching on the top surface.

The sample in the bottom of prism A (ground 260–280 mm from the top) has a lower free alkali content than the two samples above it (ground 220-260 mm from the top). This can be explained by the fact that the bottom sample includes the bottom surface of the prism that is directly over water. On both the top and bottom surface of the prism more leaching is indicated, this is as expected as the surfaces experiences a high relative humidity and possibly condensation of water. Leaching is more clearly indicated in the bottom surface this could be due to this surface being closer to the bottom of the container and closer to the water. This can also be due to drying and wick action that has redistributed the alkali close to the surface and caused an increase in alkali content in the top and bottom samples.

The free alkali content measured in the length profile from prism W is given in Figure 33. Since the prism is wrapped I would expect this to minimize the phenomenon of alkali transportation on the surface as in prism A, but this does not explain why I measure less free alkali in the bottom, than the middle. One explanation could be that the top and bottom surface was not wrapped. This seems probable as the measured free alkali content in the top is close to the average free alkali content in the middle profile. Again, the bottom surface is exposed to a high relative humidity, and this may have caused alkali to leach out on the bottom surface. However, if wick action due to drying has transported alkali to the top surface, the alkali content in the top surface could have been lower there directly after exposure. This could indicate leaching in the top surface as well. This would be consistent with UV photos of plane polished sections of wrapped prisms in Lindgårds PhD (2013), where very little cracking is seen in both the top and bottom part of the prism.

5.7 Alkali release from aggregates

Lindgård measured that prism S had leached out more than 100% of the alkali in the cement, and therefore the question of this could be caused by alkali release from the aggregates themselves was raised in chapter 2.1. The results do not have conclusive evidence to support such a claim. First, the error of Lindgård's measurements are considerable, and based on the measurements the prism may have leached 98% of the original alkali content.

The methods used in this study cannot prove whether there has been alkali release from the aggregates or not. If I had a reliable way to measure the total alkali content in the prism, as I had hoped that HAE would do, I could have calculated that 50-60%[7] of the measured total alkali content would represent the theoretical free alkali content. From this, I could have calculated the release from aggregates as the difference between the free alkali content in the sample measured with CWE and the theoretical free alkali content, see equation 34. However, as the HAE results do not give the total alkali content, this is not possible. In future studies, I would recommend using x-ray fluorescence to measure the total alkali content.

$$\left(Na_2O_{eq,cem,total} * 50\text{–}60\%\right) - Na_2O_{eq,cem,free} = Na_2O_{eq,release\ from\ agg} \qquad [34]$$

With:

- $Na_2O_{eq,cem,total}$, the total alkali content
- 50-60%, the percentage of the total alkali content in the pore water
- $Na_2O_{eq,cem,free}$, the free alkali content measured using CWE
- $Na_2O_{eq,release\ from\ agg}$, the theoretical amount of alkali released from aggregates

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[7] The free alkali content is approximately 50-60% of the total alkali content in CEM I according to Plusquellec et al. (2017).

6 Conclusion

In my master thesis project, I have investigated four concrete prisms tested with different performance tests. My objective was to determine and visualize the alkali content of the prisms to prove alkali leaching and ingress, and investigate whether a part of the alkali measured originate from the aggregates. I have also investigated error sources and calculated errors for all measurements.

My results indicate leaching and ingress in the bulk measurements, but due to drying and old age the alkali profiles are non-conclusive evidence of the alkali distribution in the prisms. However, I do recognize differences in alkali content along the length of the prisms which can be attributed to alkali transportation mechanisms.

From the discussion, I present these conclusions:

- The errors of the alkali leaching calculations are considerable for the submerged prisms S and the alkali wrapped prism W
- Thermogravimetric analysis (TGA) is a good tool for investigating the paste content in the collected samples, this in turn ensures that the contribution from aggregates can be accounted for.
- HAE is not a suitable method to measure the total alkali content, due to the large and variable contribution from aggregates.
- CWE measures free alkali content, but I have measured less than the expected 50-60% of expected alkali content as reported by Plusquellec et al. (2017), only 24-44%. However, the results are consistent and less affected by the contribution from aggregates.
- Alkali leaching and ingress is evident from the bulk free alkali measurements
- The middle profiles do not give conclusive evidence of leaching or ingress due to drying, wick action and redistribution of the alkalis. Therefore, they are not suitable for visualization of alkali distribution in a concrete prism
- The length profile indicates more free alkali in the bottom than the top of prism ASTM (A), which has experienced leaching. This can be caused by alkali transportation from the top to the bottom on the surface of the prism. In the wrapped prism (W), which has experienced ingress, I measure less free alkali in the bottom of the prism than in the middle and top. This can be due to the wrapping only covering the circumference of the prism and not the top and bottom surfaces. This can have caused alkali leaching in the top and bottom surface of the prism. The top and bottom samples of the length profiles should also be considered unreliable because of redistribution of alkalis due to drying during long term storage.
- The methods used in this study (CWE and HAE) cannot prove alkali release from aggregates.

7 Further research

The work done in this master thesis could be continued using other materials and methods. I would recommend focusing on one concrete prism test known to cause leaching, such as RILEM AAR-4.1. By casting a set of new prisms, the problem with drying and wick action during storage would be avoided. It would be interesting to profile grind the prisms after different exposures, i.e. take one prism out of the CPT-container after 1 week, one after 2 weeks, and one after 4 weeks. This could make visualizing leaching easier. As concluded, HAE is not suitable to measure total alkali content, and without that it is not possible to determine release from aggregates. I would recommend using XRF to determine the total alkali content. It would also be interesting to scan sawn surfaces of the prisms with µXRF to visualize the alkali distribution.

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9 Appendix A1

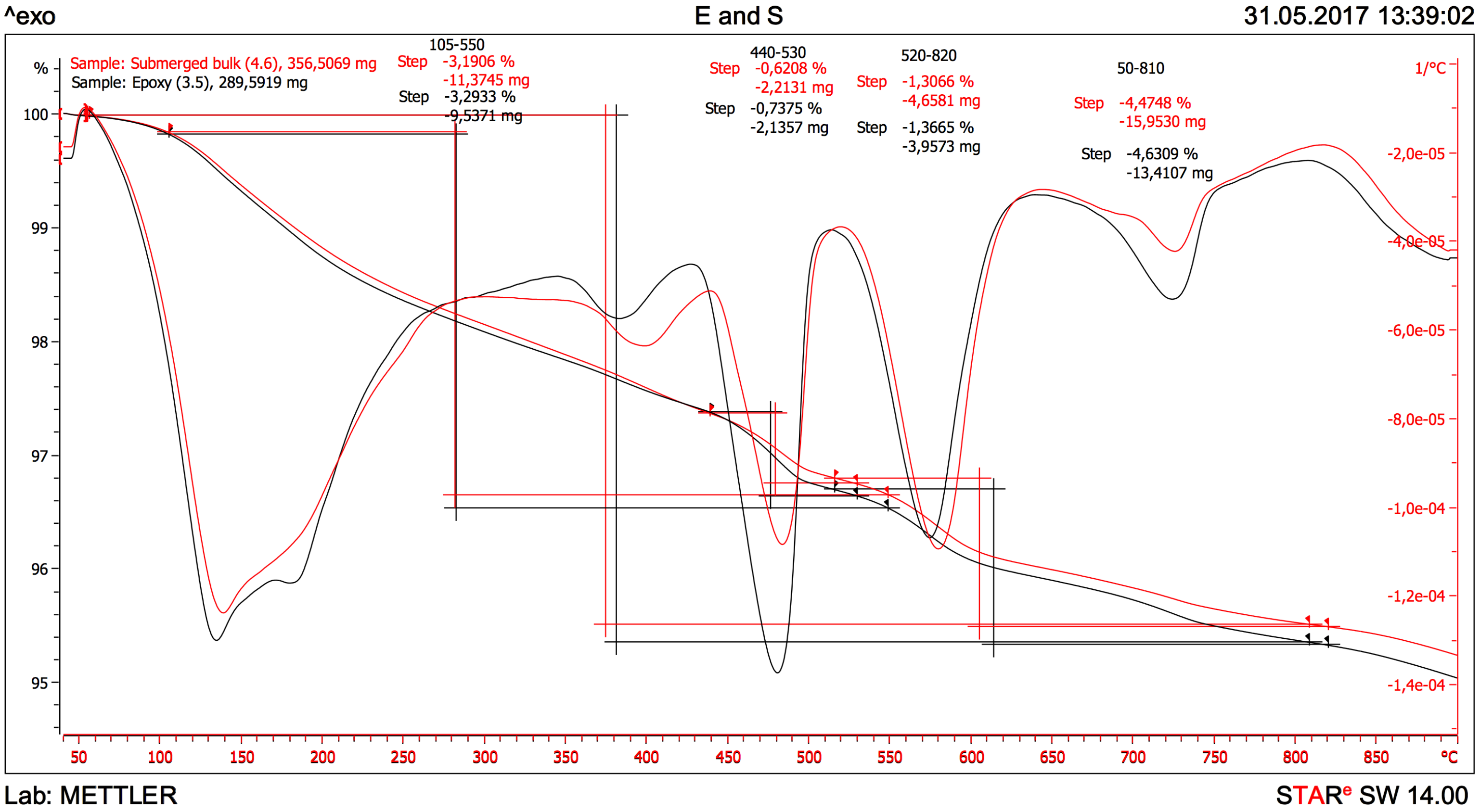

Figure 36, TGA evaluation, bulk samples, prism E and S

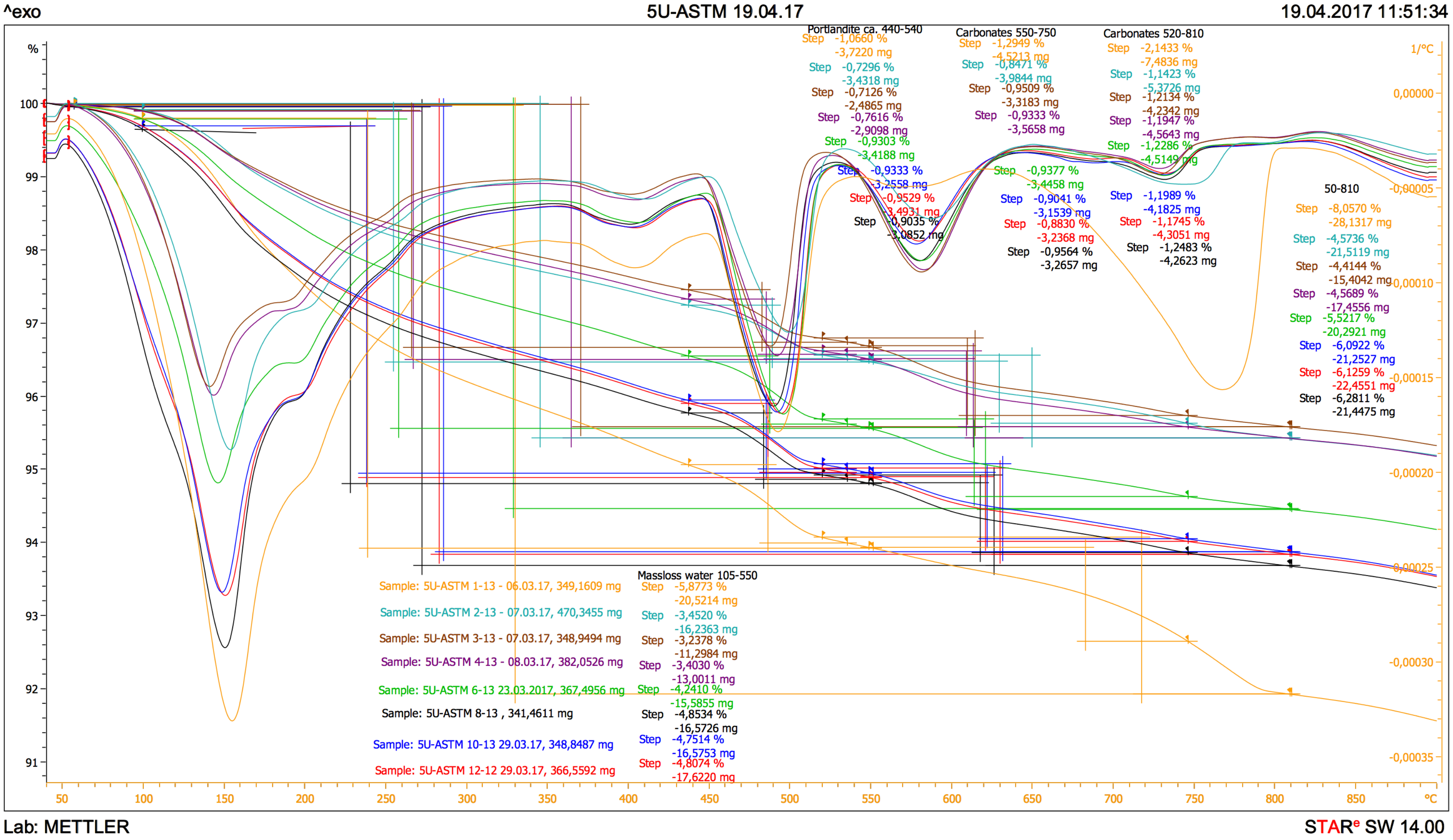

Figure 37, TGA evaluation, middle profile samples, prism A

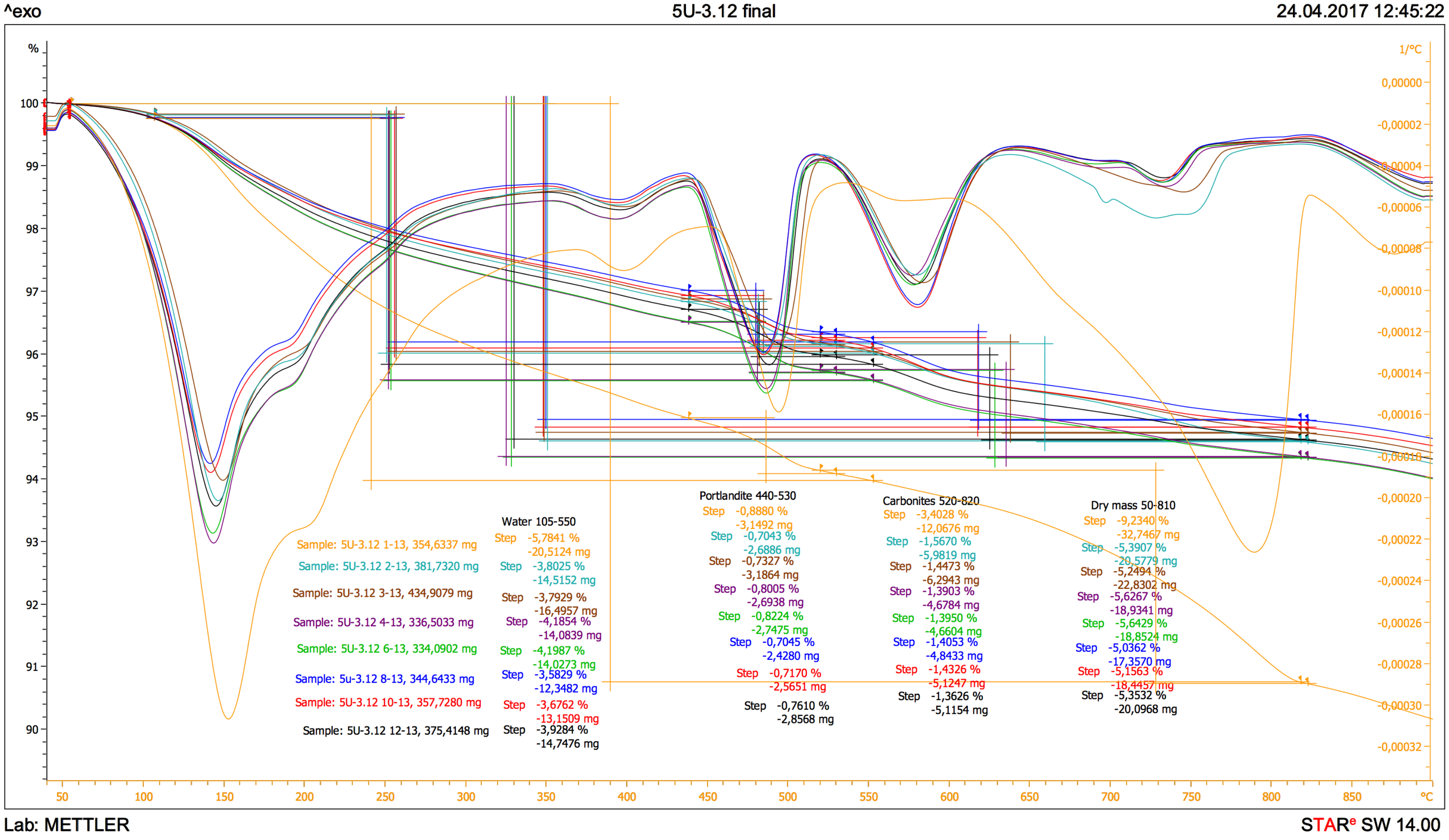

Figure 38, TGA evaluation, middle profile samples, prism W

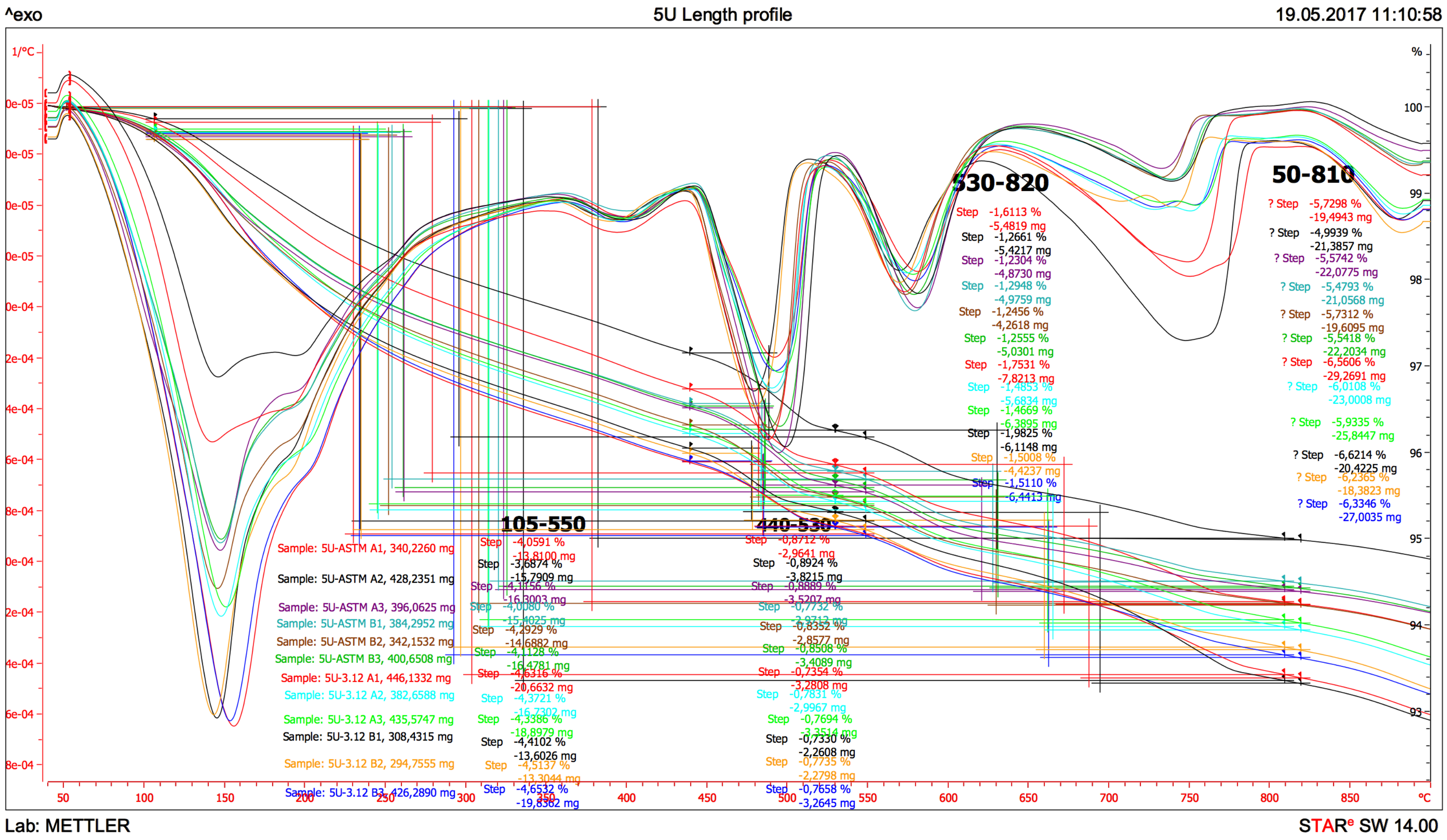

Figure 39, TGA evaluation, length profile samples, prism A and W

10 Appendix A2

The excel files with all calculations are available. Contact Peter Holiman Kermit, Klaartje De Weerdt, Jan Lindgård or Gilles Plusquellec.