



Norwegian University of  
Science and Technology

# Adsorption Isotherms for Lignosulfonate in Cement with Fly Ash and Blast Furnace Slag

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Submission date: June 2016

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Report title: Adsorption Isotherms for Lignosulfonate in Cement with Fly Ash and Blast Furnace Slag	Date: June 10, 2016		
	Number of pages (incl. appendices): 95		
	Master Thesis	X	Project Work
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In this study the adsorption of lignosulfonate, a well-known superplasticizer, on binders is investigated. Different binders are thought to affect adsorption differently, so adsorption is tested on cements with and without fly ash and ground granulated blast furnace slag. The goal is to better understand the effects of different binders on the adsorption of lignosulfonate through evaluation of adsorption isotherms obtained experimentally.

Paste samples with a w/b-ratio of 0.4 by volume with different binders are tested for lignosulfonate adsorption using UV-spectroscopy analysis. Two cements (ANL and CX) with and without the addition of fly ash and ground granulated blast furnace slag in replacement levels 30% and 60% were used. The lignosulfonate consumption is tested both for immediate addition with water and 10 minutes delayed addition to a fresh paste; the concentrations ranged from 0.05 to 1.5 g lignosulfonate / 100 g binders. Adsorption isotherms are then determined and compared to evaluate the contribution from the mineral admixtures. To investigate the correlation between the pH and consumption, pH measurements were performed on the pastes.

The consumption on blended cements with fly ash and ground granulated blast furnace slag in this study are shown to have the same consumption behavior as neat cements. There are some differences between the different binders, but the standard deviations obtained is larger than the impact of these mineral admixtures, making it hard to conclude any significance from them. The cements also have small, though significant differences in lignosulfonate adsorption. ANL seems to adsorb more than CX, especially for higher concentrations of lignosulfonate. The most apparent difference is a result of addition method: the immediate addition of lignosulfonate together with water more than doubles the amount adsorbed compared to 10 minutes delayed addition after wetting for many samples. Immediate addition shows a linear form in the adsorption isotherms, while delayed addition for most part can be described with the Langmuir model. There is also no apparent correlation between pH and adsorption of

lignosulfonate.

It is therefore clear from the experimental results that the addition of fly ash or ground granulated blast furnace slag neither increases or decreases the consumption significantly compared to neat cements. Although the materials are different, they seem to behave similarly in lignosulfonate consumption. Other parameters, such as addition time, have a far more significant effect.

Keywords:

1. lignosulfonate

2. adsorption isotherm

3. cement

4. mineral admixture

# Preface

This master's thesis was written during the spring of 2016 at Norwegian University of Science and Technology (NTNU), Department of Structural Engineering, and concludes my five year Civil and Environmental Engineering degree. The thesis was written with Klaartje De Weerd as the main supervisor.

Through the work of this thesis, I have gained a broader understanding of the effect and consumption of superplasticizers added in cement with fly ash and blast furnace slag. The consumption of lignosulfonate has been explored on site at the new lab at NTNU, Trondheim. During the autumn of 2015, I completed the paper '*Adsorpsjonsisoterm for plastiserende tilsetningsstoffer*' on adsorption isotherms for two superplasticizers in OPC. This master's thesis is a continuation of the previous study, and was completed in 20 weeks. This thesis constitutes the subject TKT4925 - Concrete Technology, Master's Thesis, which is a course of 30 ECTS points.



# Acknowledgments

I am highly grateful to my main supervisor, Klaartje De Weerd, for her valuable guidance and cooperation throughout the process. Her encouragement and useful critiques were greatly appreciated.

I would also like to extend my appreciations to my co-supervisors Alessia Colombo for her support in the lab and with experimental data, and Mette Rica Geiker for her appreciated reviews of this thesis.

Trondheim, June 2016

Marius Ekanger Aasheim





# Abstract

Plasticizers are used to increase the workability of cement in its fresh state. When adding plasticizers to a paste, the molecules chemically adsorb on the surface of cement particles. This interaction between the plasticizer and binders is complex and depends on several parameters, including cement type, addition of mineral admixtures and method of addition.

In this study the adsorption of lignosulfonate, a well-known superplasticizer, on binders is investigated. Different binders are thought to affect adsorption differently, so adsorption is tested on cements with and without fly ash and ground granulated blast furnace slag. The goal is to better understand the effects of different binders on the adsorption of lignosulfonate through evaluation of adsorption isotherms obtained experimentally.

Paste samples with a w/b-ratio of 0.4 by volume with different binders are tested for lignosulfonate adsorption using UV-spectroscopy analysis. Two cements (ANL and CX) with and without the addition of fly ash and ground granulated blast furnace slag in replacement levels 30% and 60% were used. The lignosulfonate consumption is tested both for immediate addition with water and 10 minutes delayed addition to a fresh paste; the concentrations ranged from 0.05 to 1.5 g lignosulfonate / 100 g binders. Adsorption isotherms are then determined and compared to evaluate the contribution from the mineral admixtures. To investigate the correlation between the pH and consumption, pH measurements were performed on the pastes.

The consumption on blended cements with fly ash and ground granulated blast furnace slag in this study are shown to have the same consumption behavior as neat cements. There are some differences between the different binders, but the standard deviations obtained is larger than the impact of these mineral admixtures, making it hard to conclude any significance from them. The cements also have small, though significant differences in lignosulfonate adsorption. ANL seems to adsorb more than CX, especially for higher concentrations of lignosulfonate. The most apparent difference is a result of addition method: the immediate addition of lignosulfonate together with water more than doubles the amount adsorbed compared to 10 minutes delayed addition after wetting for many samples. Immediate addition shows a linear form in the adsorption isotherms, while delayed addition for most part can be described with the Langmuir model. There is also no

apparent correlation between pH and adsorption of lignosulfonate.

It is therefore clear from the experimental results that the addition of fly ash or ground granulated blast furnace slag neither increases or decreases the consumption significantly compared to neat cements. Although the materials are different, they seem to behave similarly in lignosulfonate consumption. Other parameters, such as addition time, have a far more significant effect.

# Sammendrag

Plastiserende tilsetningsstoffer brukes i betong for å øke bearbeidbarheten i den ferske fasen. Ved å tilsette plastiserende tilsetningsstoffer i sementlim vil molekylene kjemisk adsorberes på overflaten av sementpartiklene. Denne interaksjonen mellom tilsetningsstoffet og bindemiddelet er kompleks og avhenger av flere parametere, inkludert sementtype, bruk av pozzolan og tilsetningsmetoden brukt.

I denne studien skal adsorpsjonen av lignosulfonat, et mye brukt plastiserende tilsetningsstoff, på bindemiddel undersøkes. Ulike bindemidler er antatt å påvirke adsorpsjonen ulikt, så dette er undersøkt på sement med og uten flyveaske og granulert masovnsagg. Målet ved denne studien er å bedre forstå effektene ulike bindemidler har på adsorpsjonen av lignosulfonat ved å eksperimentelt finne og vurdere adsorpsjonsisotermer.

Prøver av sementlim med et v/b-forhold på 0,4 per volum med ulike bindemidler er undersøkt for adsorpsjon av lignosulfonat ved bruk av analyse med UV-spektroskopi. To sementtyper er undersøkt (ANL og CX) med og uten tilsetning av flyveaske og granulert masovnsagg i 30 og 60 volumprosent. Adsorpsjon av lignosulfonat er testet både for umiddelbar tilsetning med vann og 10 minutter forsinket tilsetning i ferskt bindemiddel. Konsentrasjonene varierer fra 0,05 til 1,5 g lignosulfonat / 100 g bindemiddel. Adsorpsjonsisotermer ble deretter funnet og sammenlignet for å kunne vurdere bidraget på adsorpsjon fra hvert enkelt bindemiddel. For å undersøke om det er en korrelasjon mellom pH og adsorpsjon av lignosulfonat, ble pH målt i prøvene.

Konsumering av lignosulfonat i sement med pozzolan ser ut til å være tilsvarende den i ren sement; det å bruke sement delvis erstattet med flyveaske eller granulert masovnsagg har i denne studien altså vist seg å gi samme adsorpsjon som ren sement. En liten forskjell ble funnet mellom de ulike materialene, men de forskjellene er mindre enn standardavvikene, noe som gjør det vanskelig å vurdere betydningen av forskjellene. Sementtypene har også små, men betydelige forskjeller i lignosulfonatadsorpsjon. ANL ser ut til å konsumere mer enn CX, spesielt for høye konsentrasjoner. Likevel er den største forskjellen i adsorpsjon å finne ved bruk av tilsetningsmetode; umiddelbar tilsetning av lignosulfonat med vann resulterer i betydelig høyere adsorpsjon, ofte dobbelt så høyt nivå sammenlignet med 10

minutter forsinket tilsetning. Umiddelbar tilsetning gir en lineær adsorpsjonsisoterm, mens forsinket tilsetning resulterer i en isoterm som kan beskrives med Langmuir-modellen. Det var ikke funnet noen korrelasjon mellom pH og adsorpsjon av lignosulfonat.

Det er derfor tydelig av de eksperimentelle resultatene i denne studien at tilsetningen av flyveaske og granulert masovnsagg hverken øker eller reduserer adsorpsjonen av lignosulfonat. Blandet sement oppfører seg altså tilsvarende som ren sement. Andre parametere som tilsetningstid har mye større effekt på adsorpsjonen.

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# Glossary of notations and terms

The cement chemist's short hand:

C	CaO
S	SiO
A	Al <sub>2</sub> O <sub>3</sub>
F	Fe <sub>2</sub> O <sub>3</sub>
H	H <sub>2</sub> O

The chemical notation of the anhydrous phases and hydrates:

C <sub>3</sub> S	3CaO · SiO <sub>2</sub>	Tricalcium silicate
C <sub>2</sub> S	2CaO · SiO <sub>2</sub>	Dicalcium silicate
C <sub>3</sub> A	3CaO · Al <sub>2</sub> O <sub>3</sub>	Tricalcium aluminate
C <sub>4</sub> AF	4CaO · Al <sub>2</sub> O <sub>3</sub> · Fe <sub>2</sub> O <sub>3</sub>	Tetracalcium alumino ferrite
CH	Ca(OH) <sub>2</sub>	Calcium hydroxide
C-S-H	3CaO · 2SiO <sub>2</sub> · 3H <sub>2</sub> O	Amorphous calcium silicate hydrate

The main hydration product of Portland cement. It can also be formed by the reaction of pozzolana with CH.

C-A-H	Calcium Aluminate Hydrate.
	The phase formed by hydration of Portland cement and CH <sup>[1]</sup> .

Additional terms and abbreviations:

AFt-phases	Calcium trisulfoaluminate hydrate. The phase formed by hydration of Portland cement derived from pure ettringite with substitution of A by F and SO <sub>4</sub> <sup>2-</sup> for other ions <sup>[2]</sup> .
AFm-phases	Calcium monosulfoaluminate. The phase formed by hydration of Portland cement derived from pure mono-sulfoaluminate with substitution of A by F and SO <sub>4</sub> <sup>2-</sup> for other ions <sup>[2]</sup> .
OPC	Ordinary Portland Cement
FA	Fly ash
GGBFS	Ground granulated blast furnace slag
SP	Superplasticizer
LSs	Lignosulfonate from softwood tree

# Chapter 1

## Introduction

### 1.1 Background

Plasticizers or water reducers, are admixtures used in concrete to change its rheological properties in the fresh state. Adding plasticizers to a concrete paste will improve workability; however, knowledge about the interaction between cement and plasticizers is important when designing a concrete mix to obtain the desired effect. The improved properties gained through use of an SP will depend on the adsorption in the cement-water interface, as well as other factors. The adsorption mechanisms for plasticizers are a complex study and they depend on, among other factors, the cement type and mineral admixtures [3, 4, 5], alkalinity [6] and addition method [7, 8]. Even though many studies have been done on this subject, the complex topic of adsorption of SP on cements is still not fully understood.

When adding SP to a cement paste, the molecules are to some degree attracted to the cement particles and chemically adsorb on the surface. However, as the cement reacts with water, the hydration reaction produces hydrates, which can result in some of the SP molecules being consumed in hydrates, a process called intercalation [9]. The SP can thus be said to be either adsorbed on the surface of particles, intercalated in hydrates or still free in the aqueous phase. The terminology *consumed* amount SP is used to illustrate the amount no longer free in the aqueous phase.

The addition time of SP to a paste can also affect the amount consumed. Since the cement particles produce early hydrates in the first minutes after wetting [4, 10-12], much of the added SP is intercalated in these hydrates. Delaying the addition of SP until after these early

hydrates are formed can result in less intercalation, reducing the amount consumed.

Adsorption isotherms are determined evaluating the amount of consumed SP as a function of the amount of added SP for a given paste and setting. Adsorption isotherms thus shows the *consumption capacity* of, e.g., an SP for different added concentrations. Comparing adsorption isotherms across different materials allows for evaluation of the significance of chemical composition in cements and mineral admixtures in consumption.

## **1.2 Objective**

The desired effect on workability from superplasticizers on fresh cement depends on several mechanisms. The replacement of OPC with mineral admixtures has become so normal that in Norway blended cements are used more than non-blended cements. Since mineral admixtures have different properties from OPC, information about and understanding of the significance on SP consumption of blended cements are important in order to evaluate the mechanisms behind it. The aim of this study is to obtain adsorption isotherms for lignosulfonate for different binders. These adsorption isotherms will be used to evaluate the different binders capacity of the consumption of lignosulfonate from softwood, a well-known SP. Different binders are thought to affect the consumption of LS. In addition, other parameters affecting consumption of lignosulfonate will be investigated. This study will focus on comparing adsorption isotherms for two cement types, ANL and CX, blended with fly ash and blast furnace slag. The addition time of lignosulfonate was reported to affect the consumption as well, so both addition at wetting and after 10 minutes hydration was tested.

The results and conclusions will help broaden the understanding of the subject, giving a better basis for selection of SP dosage for given binders. This is important to obtain the needed workability from contractors etc.

## **1.3 Summary of experimental methods**

The experimental methods include finding the adsorption isotherms for lignosulfonate in neat OPC, blended cements and pure fly ash and ground granulated blast furnace slag. Since the alkali content was reported to affect the consumption, pH measurements have

also been taken.

Adsorption isotherms were found using UV-spectroscopy analysis on cement pastes with a w/b-ratio of 0.4 by volume. After 30 minutes' hydration time, the pore water was extracted and analyzed to find the remaining non-consumed amount of lignosulfonate. Then the consumed amount, i.e. adsorbed and intercalated amount, of lignosulfonate could be calculated. The replacement with fly ash and ground granulated blast furnace slag was 30% and 60% by volume. Lignosulfonate was added in dosages of between 0.05 and 1.5 g lignosulfonate / 100 grams binder. pH measurements were done on the pore water using a pH meter. Repeatability measurements were also taken to indicate the accuracy of the methods.

## 1.4 Hypotheses

The consumption of LS on composite cement is complex and dependent on several factors. Finer particles have more surface area for reactions with lignosulfonates <sup>[13]</sup>; this parameter contributes to CX and fly ash achieving higher consumption than ANL and ground granulated blast furnace slag. Since a lower pH in the paste has shown to increase lignosulfonate consumption <sup>[6]</sup>, the addition of FA, which reduces the pH <sup>[14]</sup> may contribute to increased consumption on binders. Different chemical composition also affects the consumption. The aluminat phase, C<sub>3</sub>A, with its immediate generation of early hydration products after wetting <sup>[15, 16]</sup> allows for a larger intercalation of LS than the other main calcium phases. A high C<sub>3</sub>A content will see a high consumption compared to binders rich in calcium silicate minerals. CX has almost 3 times as much C<sub>3</sub>A as ANL, so one of the hypothesis is that this cement will consume more LSs than ANL. As the hydration process begins only moments <sup>[4, 8]</sup> after wetting, new surface area is generated for consumption. Based on this it is thought that immediate addition of lignosulfonate should produce higher consumption than delayed addition, since in the latter case the early hydrates have already been produced.



# Chapter 2

## Theoretical background

### 2.1 General

When adding plasticizer to a material, be it cement, paint or other products, the aim is to increase workability and fluidity. The long molecules of a plasticizing admixture usually work by wrapping themselves around the dispersants in the material, resulting in the desired effect <sup>[17]</sup>. The adsorption of the plasticizers on the outer layer of the dispersants is necessary for them to give the effect. Replacing some cement with mineral admixtures also affects the adsorption <sup>[18]</sup>. Although many studies have been done on this subject, the mechanism behind this phenomenon is complicated and still not fully understood. The subject of SP consumption will begin with general theory of cements and mineral admixtures before the nature of plasticizers and lignosulfonate are explained. The theories of interaction between lignosulfonate and binders will then be explained in light of adsorption isotherms, rheological properties and mechanisms and factors responsible for the consumption of lignosulfonate.

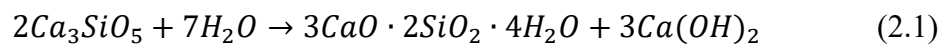
### 2.2 Cement and chemical compositions

Cement is a complex mixture of several different compounds. One manufacturer may produce a cement with a different composition from that of another producer, giving many possibilities when designing a mix, and also complicating the process of evaluating mechanisms in reactivity etc. since there is variation between studies.

Even though the chemical composition of cement varies, most of it can be divided into four phases (compounds): alite, belite, aluminate and ferrite. These phases have different effects

on the mechanisms to be controlled. When analyzing a cement, the specific composition must therefore be considered when calculating the amount of needed admixtures, water demand, liberated heat etc.

When cement is exposed to water, the hydration of the particles begins. As the process advances, the strength of the cement or concrete increases. This is mostly a result of the formation of calcium silicate hydrate (C-S-H), the main product of the hydration. This reaction can be expressed by the formula 2.1 <sup>[19]</sup>, although it should be mentioned that this is an approximation since the C-S-H gel is formed in several different varieties <sup>[20]</sup>.



Another phase largely produced during cement hydration is ettringite, a product of C<sub>3</sub>A and 3 CaSO<sub>4</sub>, formula 2.2 <sup>[21]</sup>. High content of C<sub>3</sub>A in the cement results in more ettringite during early hydration. Ettringite is an AFt phase, and may later convert to the AFm phase.



As cement is wetted, positive ions such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup> are dissolved from the surface into the aqueous solution. This leaves the cement particles with a negative surface charge with O<sub>4</sub><sup>3-</sup>, AlO<sub>3</sub><sup>3-</sup> remaining <sup>[13]</sup>

## 2.3 Mineral admixtures

Proper use of mineral admixtures can improve the concrete's properties in several ways, as the pore structure developed by these minerals is much finer than for ordinary Portland cement (OPC) <sup>[22]</sup>. As the pores become finer, the concrete is also more durable to chemical attacks and reinforcement corrosion. The microstructure is shown to be dependent of alkali-activation of the minerals <sup>[23]</sup>.

The increased use of mineral admixtures has resulted in the need of further data regarding the properties of concrete blended with these materials. The recent years have seen a rise of their use, mostly due to economic and environmental interest. For example, FA can cost



half of what cement does. Replacing a portion of the cement with a mineral admixture also ends up with less carbon dioxide from cement production, while the mineral admixture is being used instead of ending landfills <sup>[3]</sup>.

### **2.3.1 Fly ash**

Fly ash, a byproduct of coal-fueled power plants, is a powder that often replaces some of the cement used in concrete in order to obtain wanted properties. Since FA often is a byproduct of production, the properties are not characterized and defined on a general level <sup>[24]</sup>, and they can vary depending on producer and method of production. The descriptive particle model for FA is that it should be spherical, thus having the lowest surface/volume-ratio possible. NS-EN 450 divides it into most used classes, including FA class F made from burning anthracite or bituminous coal, FA class C from burning lignite or sub-bituminous coal.

### **2.3.2 Ground granulated blast furnace slag**

When separating a metal from its raw ore, one of the by-products is ground granulated blast furnace slag. GGBFS, being a mixture of metal oxides and lime, is used as a pozzolan in cement. GGBFS also varies from one batch to another, so the compositions are not defined by a precise chemical content. Even though many of the properties are shared with FA, they do differ in selected areas. GGBFS is usually a coarser material than FA, and the chemical composition is different.

## **2.4 Plasticizing admixtures**

The ease with which concrete and cement can be placed and compacted depends on, among other factors, the workability. Many factors contribute to the workability of cement, such as water content, cement composition and SP. Different SP are available on the market, giving us a range of choices when designing concrete. According to NRMCA <sup>[25]</sup>, the global cement production in 2010 was 3.4 billion tons. If we assume usage of plasticizer on average 0.3 wt% of cement, a calculated amount of 10.2 million tons of plasticizer are demanded. The usual dosage requirements for superplasticizers are 0.5 to 3.0 wt% of cement <sup>[26]</sup>.

### 2.4.1 Interparticle forces

The fluidity of cement is a function of, among others, the repulsive force between particles, since these repulsive forces reduce internal friction. The particles have an attractive force, called van der Waals force, and an electrostatic repulsive force. The electric charge can change when plasticizers are added into the mix <sup>[27, 28]</sup>. SPs have a strong negative charge, increasing the electrostatic repulsion. The zeta potential, which is the potential difference between the slipping surface and the solution, is reduced as the negatively charged LS molecules form a layer at the surface. Particles with a low zeta potential repulse each other, resulting in a lower internal friction and higher workability, also affecting the adsorption mechanism <sup>[29]</sup>.

Another force present is the steric repulsive force, generated by the gain of size and density of the particles when long polymer chains such as LSs are adsorbed on the surface. The large size of the polymer takes up a certain amount of space in the solution. If another particle with or without the same polymer chains is brought too close, the cost in energy increases as the distance decreases. This leads to the steric effect, which increases plasticizing action.

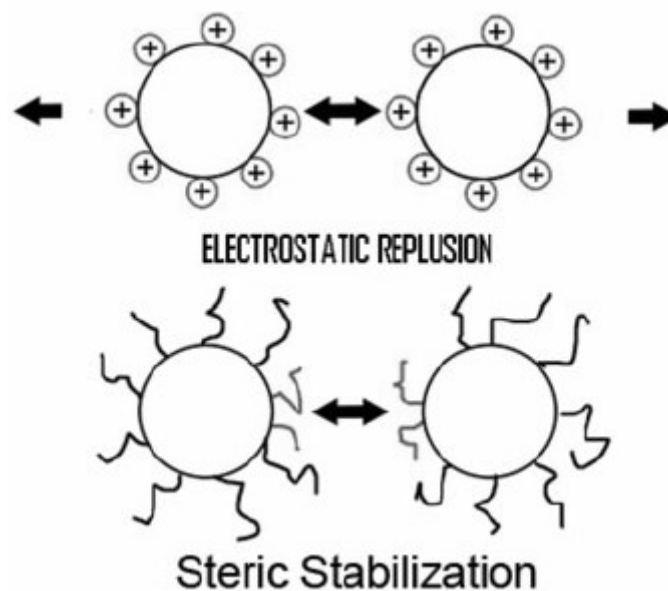


Fig. 2.1. Electrostatic repulsion and steric stabilization, picture representing two dispersants (cement particles) with adsorbed plasticizers <sup>[30]</sup>.

It is also said <sup>[17]</sup> that cement particles, when wetted, have a tendency to flocculate,

meaning they group up as larger particles. These flocculated particles tend to trap or bind water in the system, so that the free-water content is lowered. Plasticizers will, through dispersion mechanisms, deflocculate and free the water trapped. This results in a higher effective w/b ratio, as well as lower interparticle friction since the larger flocculations increases the friction in the solution compared to dispersed cement particles.

The plasticizer works as a dispersant, being able to deflocculate cement particles, keep free particles dispersed <sup>[17]</sup>, reduce the zeta potential of the dispersants <sup>[31]</sup> and give a steric hindering effect, all which results in a higher workability.

The explanation of the effect on rheology from fine *mineral admixtures* has been hypothesized and discussed in several papers; however, there is general consensus that the rheological effect comes from, among others, the filling role and ball bearing effect <sup>[32, 33]</sup>, as explained below:

Large cement particles themselves cannot fill the void between them in paste. As long as this void stays vacant, free water in the solution will take up the space. However, much as cement particles are able to fill up the void between the aggregates, smaller pozzolanic particles are able to surround the cement particles, thus explaining *the filling role*. As mentioned, pozzolanic particles may be several orders of magnitude smaller than cement particles. Filling up the void reduces the water previously between the particles, resulting in being able to lower the water content and keep the same fluidity.

The ball bearing effect is another way that mineral admixtures can reduce internal friction. The large uneven cement particles in a solution will collide from time to time, and these impacts increase the yield strength and reduce the workability in the paste. When small pozzolanic particles are also a part of the paste, they surround the larger cement particles, hindering their contact and making them easily “roll” over each other due to the spherical shape of the pozzolanic particles. This reduces the friction between cement particles in a solution, giving the paste higher workability and fluidity.

Pozzolanic materials have a finer, spherical shape <sup>[3]</sup>. The sphere has the highest volume/surface ratio of all shapes, minimizing the water needed for surface activity, which has a positive effect on rheology, even though they are smaller than cement particles.

### 2.4.2 Lignosulfonate

Lignosulfonates, or sulfonated lignin, is used as adhesive, dye dispersant and most prominently as a superplasticizer in concrete. The chemical is a product from processing and producing wood pulp through sulfite pulping. With 50 million tons of industrial lignin produced every year, only 10% is used, with most of it being untreated. The molecule of a LS contains both hydrophobic groups (carbon chain) and hydrophilic groups (sulfonic phenylic hydroxyl and alcohol hydroxyl) <sup>[34]</sup>, see Fig. 2.2. As a result of lignin production, LS may be derived from different wood species. Since LS has a negatively charged  $\text{-COO}^-$  group <sup>[35]</sup> it will tend to electrostatically attract positive charged particles or ions in a solution. The LS molecule often contains sugar, a well-known retarder for cement hydration.

As the lignin molecule is a large, complex polymer, Fig. 2.3, the resulting LS molecule may have large chains that are chemically bound to the surface of cement particles while polymer chains float around the particle. These large polymers have the added dispersing effect of steric hindrance in addition to electrostatic repulsion <sup>[4]</sup>.

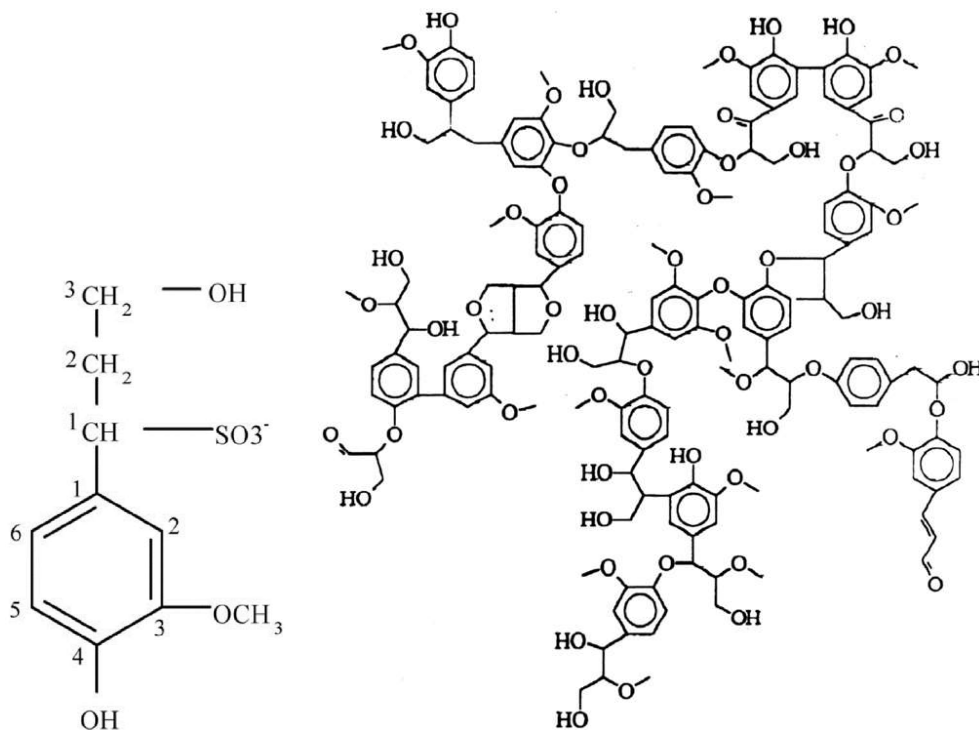


Fig. 2.2 (left). Example of structural unit of lignosulfonate

Fig. 2.3 (right). Structure of a lignin polymer <sup>[36]</sup>

## 2.5 Adsorption isotherm

Adsorption, i.e. the adhesion of molecules to a surface, creates a film of the *adsorbate* on the surface of the *adsorbent*. Flatt & Houst (2001) <sup>[9]</sup> reported that plasticizers after addition could be in three different states: a) being adsorbed on the outer surface of cement particles, b) consumed by intercalation or c) still dissolved in the aqueous phase.

Consequently, this means that equal dosage may give different effects depending on the factors influencing the adsorption mechanism. As explained, the surface-adsorbed plasticizers change the zeta potential in an advantageous way. Preferably little should be intercalated or free in the solution, as these polymers give little or no effect on workability. Even though the rheological effect of plasticizers in the aqueous phase is debated, it is accepted that this effect is much smaller than the effect from adsorbed plasticizers <sup>[9]</sup>.

As mentioned previously, the terminology *consumed* amount accounts for the sum of the amount of SP that is adsorbed on the surface of particles or intercalated in hydrates. When adding SP to a paste, some of the molecules will be consumed, and some will be free in the aqueous phase, depending on the factors influencing consumption. The relationship between added amount SP and consumed amount SP are depicted graphically through graphs called adsorption isotherms. These graphs show the adsorption of an SP as a function of added amount of the SP, often in percentage of mass per binder.

Several different “types” of adsorption isotherm have been named, thereby categorizing the different effects. The consumption behavior of a sample can change according to an increase of addition of SP. As the adsorbate reacts with the adsorbent, the concentration of free adsorbate left is reduced in the medium. Le Châtelier's principle states that the solvents will direct the equilibrium to reduce the influence of adding more adsorbates; i.e., the adsorption reaction will continue until equilibrium is reached. While adding more adsorbate can result in increased adsorption, diminishing returns might occur after a certain concentration.

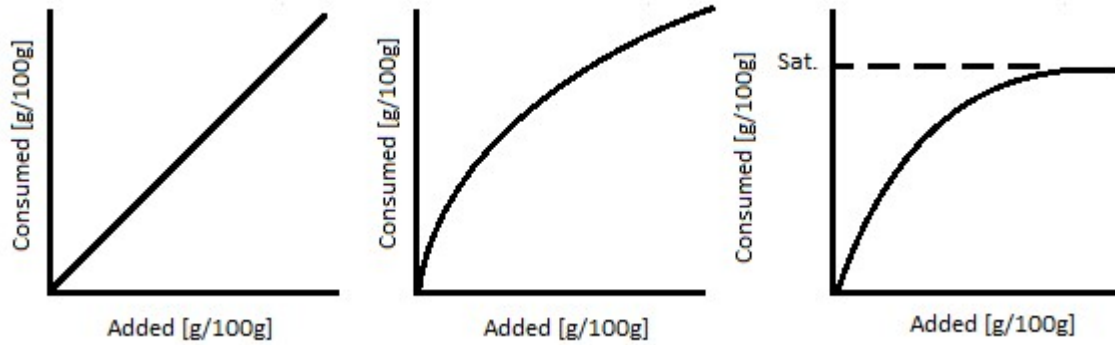


Fig. 2.4. Adsorption isotherms for cement-plasticizer adsorption. Linear isotherm (left), Freundlich isotherm (middle) assumes multilayer adsorption without a defined plateau and Langmuir isotherm (right) assumes single-layer adsorption with a saturation point.

One of the adsorption isotherm is the Freundlich isotherm, Fig. 2.4. This isotherm can describe systems wherein the adsorbate is able to function in a multilayer. With multilayer adsorption, the polymers can adsorb onto each other after the cement surface is fully adsorbed. As the adsorbed concentration increases, an even higher added concentration is needed to obtain the same amount of adsorption due to the repulsion of the already formed adsorbates. The Freundlich isotherms can mathematically be expressed as

$$\frac{x}{m} = K \cdot p^{1/n} \quad (2.3)$$

where

$x$  is the mass of the adsorbate

$m$  is the mass of the adsorbent

$p$  is the equilibrium pressure of the adsorbate

$c$  is equilibrium concentration of the adsorbate in the aqueous solution

$K$  and  $n$  are constant depending on the chosen materials.

Another way of assuming adsorption is through the Langmuir adsorption isotherm, Fig. 2.4. This model considers the adsorbents to have finite distinct sites available for adsorption, which does not allow the molecules to react with each other or form other systems besides a single layer adsorption. With this model, the adsorbate only has one layer of adsorption on the adsorbent; i.e., one adsorbate not overlaying another adsorbate. Thus, after a certain saturation concentration, the addition of more adsorbates should not

result in more adsorption. The Langmuir isotherms can be expressed mathematically as

$$\theta = \frac{K \cdot P}{1 + K \cdot P} \quad (2.4)$$

where

$\theta$  is the number of sites covered with adsorbents at equilibrium

K is the equilibrium constant

p is the adsorbate pressure concentration

## 2.6 Parameters influencing adsorption of LSs

Many studies on adsorption of LSs, among others, highlight the contributions of the different mechanisms behind it. Several mechanisms are responsible for adsorption, including addition time, chemical composition, early hydrates fineness and pH. The term *consumed* amount will be used to describe the amount of LSs that is *not* free in the aqueous solution; i.e., the amount of LSs that is intercalated in hydrates, adsorbed on the surface etc.

### 2.6.1 Chemical composition

The consumption varies between the different cement minerals. When estimating the consumption of a given dosage LS, one should consider the chemical composition of the binder. The content in Portland cement is mainly the C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF phases. As shown by Cabrera and Rivera-Villarreal (1999) <sup>[15]</sup>, the amount LS consumed on the surface of the different clinker minerals is lowest for C<sub>3</sub>S, higher for C<sub>4</sub>AF and highest for C<sub>3</sub>A. Even though the reactivity is much larger for C<sub>3</sub>A than C<sub>3</sub>S, the total gained adsorption may not be highest for C<sub>3</sub>A when considering that the mayor constitution of cement is C<sub>3</sub>S, while C<sub>3</sub>A counts for a lesser percentage of weight. Free lime in the cement seems to consume more plasticizer than calcium silicate <sup>[4]</sup>. Free lime is mostly CaO and Ca(OH)<sub>2</sub>. When dosing plasticizers, a high lime content will reduce the amount in the aqueous solution, since a larger percentage will be consumed. Using lignin sulfonic acid <sup>[5]</sup> to test consumption on the four main clinker minerals, Hanehara & Yamada (1998) show that the consumption is about 80% higher on C<sub>3</sub>A and C<sub>4</sub>AF than on C<sub>2</sub>S and C<sub>3</sub>S, due to

the accelerated hydration of the two latter phases.

As for the rheological study of the importance of chemical composition in cement, Vikan (2005) <sup>[4]</sup> proposes a correlation between flow resistance and chemical properties in the cement. Studying the particle surface area or chemical composition alone yields little linear correlation with flow resistance. This is thought to be a result of the *many* properties affecting flow resistance, such as the particle surface area and chemical composition. When the sum of aluminate surface area multiplied by the relative chemical reactivity of C<sub>3</sub>A and the calcium silicate surface area multiplied by the relative chemical reactivity of C<sub>3</sub>S was studied, a linear correlation with the flow resistance was found. The function studied shows the total surface reactivity of the cement, weighted for reactivity of the minerals. This result may be used to model a technique for estimating the consumption of plasticizers. Even though a linear correlation between consumption and flow may not be apparent, this shows that the chemical composition *together* with the physical properties, such as particle surface area, gives a more accurate basis for evaluation than just evaluating the properties alone.

### **2.6.2 Effect of pH**

The pH in a paste is shown to affect the consumption when containing LS. K. R. Ratinac et al. <sup>[6]</sup> studied how the pH in a paste controls other parameters, like LS consumption. Three samples were analyzed with measured pH values of 9.2, 6.0 and 3.0. They found that the amount consumed LS *increased* for *decreasing* pH, Fig. 2.5. It was reported that the consumed amount about halved for each three-unit increase in pH in the paste. The findings were assumed to have several reasons. Mainly, the decrease of consumption is a result of high poly-electrolytic expansion with increased pH. Poly-electrolytic expansion increases the amount of surface space occupied per polymer so that less LS can adsorb on the same area.



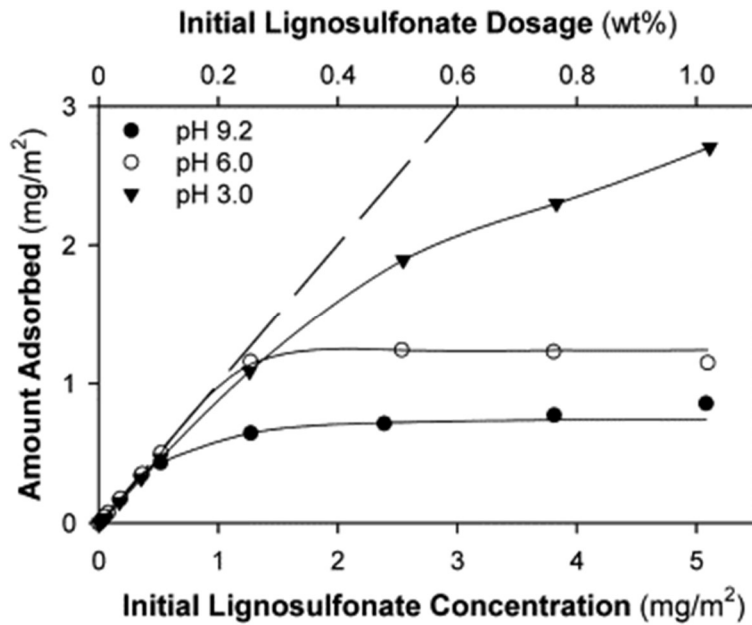


Fig. 2.5. Adsorption isotherms for lignosulfonate with varying pH. (Ratinac et al. <sup>[6]</sup>).

The pH in a paste is dependent on the binders used. Another study <sup>[14]</sup> tested the significance of FA on three different cements. For all samples, the addition of 30% FA decreased the pH and the consumption of LS was increased. They found that the higher consumption when adding FA can partly be contributed to the lower pH in the paste.

### 2.6.3 Early hydrates

The hydration products produced will also affect the consumption mechanisms. For early hydrates, the most significant hydration product is ettringite. AFm, portlandite and gypsum are also present in early hydrates. Since the different products have different zeta potentials and thus different reactivity with LS, the composition of the cement and mineral admixtures will have an impact on the hydrates and consumption. Through experiments with different hydration phases <sup>[31]</sup> the results show that AFt has a high zeta potential of 4.15 mV, AFm has an intermediate value of 2.84 mV, while portlandite and gypsum have values far below zero and close to zero respectively. The consumption amount was also tested in the same experiment. The results show that the adsorption of several SP was highly dependent of the zeta potential. The AFt consumed far more than AFm, while the consumption of portlandite and gypsum was unmeasurably small.

When cement gets wetted, the C<sub>3</sub>A phase immediately starts the hydration process and it experiences a “flash set” unless gypsum is added. When the early hydrates of C<sub>3</sub>A grows,

the surface of these particles are undergoing continuous renewal. The surface-adsorbed LS will then be consumed by the hydrates, allowing for new sites for additional adsorption of LS. The result is a high amount of consumed LS in C<sub>3</sub>A hydrates, while the LS left in the aqueous solution tends to adsorb on the more dormant phases (e.g. C<sub>3</sub>S and C<sub>2</sub>S). This forms a layer on the surface of these phases, further retarding the hydration. It was shown by Ramachandran (1972) <sup>[37]</sup> that the inhibition of hydration on C<sub>3</sub>S from LS occurs when the added concentration exceeds 0.25%. Although it is noted that this is a complex function of several other factors, it is also shown that when the concentration of LS is low, C<sub>3</sub>S hydration proceeds and is able to increase the consumption of the polymer. When the concentration of LS is higher, the hydration of C<sub>3</sub>S is negligible and as a result the uptake of LS from the solution is reduced. However, when C<sub>3</sub>A is also added, the amount LS in the solution is depleted quickly enough so that the C<sub>3</sub>S hydration begins again. This shows that a higher C<sub>3</sub>A/C<sub>3</sub>S relationship should result in a higher consumption capacity.

Fly ash and GGBFS have been basic ingredients in cements for a long time, also in conjunction with SP. Knowledge about the consumption mechanisms for mineral admixtures is crucial for determining processes on consumption in composite cements. As mentioned, FA and GGBFS have different particle structures when compared to OPC.

Lignosulfonates have negatively charged anionic groups, making them electrostatically attracted to positively charged particles. Fly ash is a negatively charged material, while OPC can form a positively charged surface layer <sup>[38]</sup>. This affects the consumption process and amount of consumed LS in FA blended cements. OPC has more sites with positive zeta potential (OPC has more calcium compared to FA), and accordingly more area for LS to react on than for FA. The particles and their related properties should also be considered. FA, on a particle level, is smoother and spherically shaped, while cement particles have “defects” and uneven surfaces <sup>[38]</sup>. The resulting sites for adsorption are far less for FA than for OPC.

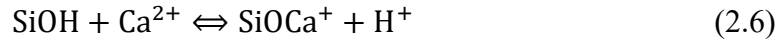
#### **2.6.4 Delaying addition**

Mixing cement with plasticizers involves adding cement powder, water and plasticizer together and stirring until a homogenous paste is produced. However, it has been shown that the time of addition of the plasticizer to the paste will affect the final workability.

When delaying the addition of plasticizers in the paste, the final rheology improves, even though the same dosage of plasticizer is used [9, 39]. Uchikawa et.al showed that the consumed quantity of several plasticizers, including LS, was higher for immediate addition compared to delayed addition. Vikan (2005) [4] also described this effect and the mechanism of delaying the addition of plasticizers. Immediately after wetting, the cement hydration produces growing hydrates on the surface, which means that the outer layer of the cement particles is continuously renewing itself. When new surface area is generated as a product of hydration, the polymers still in the aqueous phase now have new sites for adsorption [8], making it so that the particles consume a higher percentage than is possible for surface-adsorption only. When plasticizers react and adsorb on the surface of cement particles in the pre-dormant period, the cement particles form hydrates that trap the polymers in this new phase. This is called an organo-mineral phase [7] that adds to the surface of the particle. During early hydration, the polymers are drained from the solution and intercalated inside cement particles. Even though the consumption of plasticizers increases with immediate addition, the intercalated polymers produce little to no effect on workability. However, this reaction is halted after only a few minutes [4, 10-12], and polymers added after this time will adsorb on the surface to a greater extent than they are intercalated. Since a still-renewing hydrate surface intercalates the polymers added with water, delaying the addition of plasticizer reduces the effect of this phenomenon. This effect comes from the early hydrates, such as AFt, already being partially formed before addition of the plasticizer, so that little more can be intercalated. The main source of immediate hydration after wetting comes from C<sub>3</sub>A hydration. The aluminate phase, when wetted, reacts and produces rods of AFt phase. This is also shown as an initial peak in the liberated heat during hydration.

### 2.6.5 Multilayer adsorption

The surface of cement particles has a negative charge that can be altered. The silanol sites (SiOH) of this phase may either dissociate, giving a negative charge, or adsorb Ca<sup>2+</sup> ions released from inside the cementitious particles, as seen in Eq. 2.5 and Eq. 2.6. Both dissociation and adsorption reactions release H<sup>+</sup> ions [40].



The surface zeta potential will correspondingly depend on how many  $\text{SiO}^-$  and  $\text{SiOCa}^+$  groups formed, the former giving a negative zeta potential, and the latter a positive. If  $\text{Ca}^{2+}$  ions are present,  $\text{SiOCa}^+$  could be formed. The zeta potential is a key factor when considering LS adsorption on the surface. Since LS is negatively charged, a positive zeta potential allows for high adsorption, while the contrary hinder adsorption.

Free lime is a source of alkali in paste. It was shown <sup>[4]</sup> that an *adequate* amount of soluble alkali increases the compatibility between plasticizer and cement. An overly high or low amount of soluble alkali seems to decrease the fluidity of the paste. Adding alkali sulfates (in this example  $\text{Na}_2\text{SO}_4$ ) results in a higher fluidity for paste with an alkali content that was too low, and lower fluidity for cements where the alkali content already was optimal. Due to the high pH of cement (about 13), the hydration product C-S-H will gain a negative surface charge. As cement particles gain a negatively charged coating,  $\text{Ca}^{2+}$  ions from inside permeate the surface of the particles and form an “electrical double layer” around C-S-H and  $\text{C}_3\text{A}$  surfaces <sup>[35]</sup>. This new double layer is gives the particles a positive charge. Since LS are negatively charged, the  $\text{Ca}^{2+}$  layer attracts the negatively charged groups of the polymer and creates new available locations for adsorption, thus increasing the total consumption of LS.

At the negatively charged cement surface,  $\text{Ca}^{2+}$  ions tend to react and adsorb, creating a Stern layer, changing the surface charge and attracting LSs. This forms a single layer polymer at the cement surfaces. However, as previously mentioned, it is possible that a surplus amount  $\text{Ca}^{2+}$  ions may adsorb at this single-layer of polymer, thus again modifying the surface charge. This might aid the adsorption of another layer of polymer, increasing the total amount adsorption and forming a multi-layer structure <sup>[28, 41]</sup>.

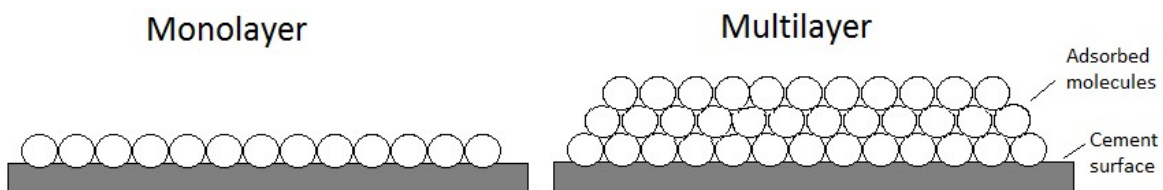


Fig. 2.6. Simplified model of monolayer and multilayer adsorption.

For the specific material lignosulfonate, determining whether monolayer or multilayer adsorption is applicable is necessary to propose a possible adsorption isotherm. Several experiments have been conducted on this topic. It has been shown <sup>[15]</sup> that the amount LS adsorbed on the surface ranges from 30-50 mg/g for C<sub>3</sub>S, 60-200 mg/g for C<sub>3</sub>A and 80-130 mg/g for C<sub>4</sub>AF. These amounts are shown to correspond to a multilayer of LS at the surface of the particles when the increase of surface through hydration is taken into consideration. Banfill <sup>[15]</sup> also points out that findings of surface-adsorbed amounts of LS demonstrate a case of a multilayer on the cement particles. It was also reported that this multilayer of polymers increases the steric dispersion effect to at least the same level as change in zeta potential. Also reported by Vikan (2005) <sup>[4]</sup>, adsorption of LS and SNF on OPC showed formation of multilayers. However, it was also noted that after a given concentration of LS a plateau was reached, meaning that no or only a little more LS would adsorb after the concentration at saturation. This saturation dosage was noted to be dependent of the particle surface area, amount of C<sub>3</sub>A and amount of soluble alkali.

### **2.6.6 Fineness**

The fineness varies greatly between different types of cements and mineral admixtures. A finer material has more surface area than a coarser material. Since adsorption of the polymer is thought to occur on the surface of the particles, a larger surface area will have more sites for reactions between the particles and polymer, resulting in a higher amount of adsorbed LSs <sup>[4]</sup>.

## **2.7 Summary**

When adding superplasticizers to a paste, the increased workability is mostly a result from surface adsorbed polymers. These polymers give the desired effect on workability from the change of electric charge on the particles, called electrostatic repulsion, and from the increase of size and density, called steric hindrance. Lignosulfonate, the SP used in this study, react with the particles immediately after wetting. The interaction between binders and LS are dependent on several parameters. The chemical composition in the paste will affect the production of early hydrates, thus intercalating polymers which increases the consumption level. Intercalation in early hydrates can be reduced when delaying addition

of LS. Consumption of LS are shown to be dependent of the pH in the paste, where reduced pH gives higher consumption. Multilayer adsorption will also give higher consumption, especially where surface adsorption is the main mechanism.

# Chapter 3

## Experimental

### 3.1 Materials

Two different cements and two different mineral admixtures have been studied in this thesis. The two cements are Norcem Anleggsement (ANL), type 52.5 N, produced by Norcem in Brevik and Kjølsvik, Norway, and Cemex (CX), type 52.5 R, produced by Cemex. The phase compositions of the two are shown in Table 3.1.

Table 3.1 – Main phases in cement ANL and CX from XRD-Rietveld analysis performed by École des Mines d'Alès, France.

Phase composition (%wt)	ANL	CX
<b>Alite</b>	60.5	54.3
<b>Belite</b>	14.2	18.8
<b>Aluminate cubic</b>	1.3	4.7
<b>Aluminate ortho.</b>	0.9	2.4
<b>Ferrite</b>	14.0	6.5

The chemical composition and physical properties for the cements and mineral admixtures are shown in Table 3.2 and Table 3.3 respectively.

Table 3.2 – Chemical composition of the raw materials

Chemical element (%wt)	Fly Ash <sup>a</sup>	GGBFS <sup>a</sup>	ANL <sup>b</sup>	CX <sup>b</sup>
Fe <sub>2</sub> O <sub>3</sub>	7.54	0.48	3.50	2.60
TiO <sub>2</sub>	0.98	0.76	0.22	0.25
CaO	4.10	42.79	62.70	64.00
K <sub>2</sub> O	2.20	0.76	0.40	1.00
P <sub>2</sub> O <sub>5</sub>	0.38	0.01	0.15	0.23
SiO <sub>2</sub>	59.37	36.15	20.60	20.00
Al <sub>2</sub> O <sub>3</sub>	21.82	11.04	4.40	4.60
MgO	2.02	7.37	1.60	2.40
Na <sub>2</sub> O	0.93	0.09	0.30	0.20
SO <sub>3</sub>	0.26	1.56	3.30	3.60
<b>Sum</b>	99.60	101.01	97.17	101.01

<sup>a</sup>analyzed at NTNU, Trondheim<sup>b</sup>analyzed by the producers

Table 3.3 - Physical properties of the raw materials analyzed in École des Mines d'Alès, France

	Fly ash	GGBFS	ANL	CX
LOI (%) 1000 °C	0.29	0	1.6	1.7
Blaine surface (m <sup>2</sup> /kg) <sup>a</sup>	300-450	327 <sup>b</sup>	360	540
Surface area (m <sup>2</sup> /kg) <sup>c</sup>	1680	776	890	1326
Density (g/cm <sup>3</sup> ) <sup>a</sup>	2.370	2.930	3.13	3.09
d <sub>10</sub> (µm)	4.0	1.0	2.0	2.0
d <sub>50</sub> (µm)	14.0	10.0	12.0	10.0
d <sub>90</sub> (µm)	54.0	34.0	34.0	26.0

<sup>a</sup>Data given by the producer.<sup>b</sup>Measured at SINTEF Materials and Chemistry, Norway.<sup>c</sup>Measured by BET analysis at NTNU, Norway.



The lignosulfonate used is from softwood and produced by Borregaard, Norway. The chemical and physical properties are listed in Table 3.4.

Table 3.4 – Chemical and physical properties of the lignosulfonate superplasticizer used

Plasticizer type	Mw	Org S	SO <sub>4</sub> <sup>2+</sup>	Ca <sup>2+</sup>	Na	COOH	φ-OH	Total sugar (%)
		(∞ SO <sub>3</sub> )	(mass%)					
LSs	29000	4.6	0.9	4.6	0.9	7.1	1.4	8.3

### 3.2 Experimental design

The aim of this study is to evaluate the consumption of LSs with different binders. To investigate whether the different binders affect the consumption of LSs, experiments on pastes with the given binders must be done. The results from these experiments will provide quantitative data that can be interpreted when comparing the binders and the likely mechanisms behind consumption.

Typical blended cements used in Norway inspired the mix design. A w/b-ratio of 0.4 by *volume* is used in all samples. Since the use of blended cements has become common, the effect on consumption when replacing 30% and 60% of cement with FA and GGBFS has been studied. Two cement types have been investigated: ANL cement and CX cement. Adsorption isotherms were found for neat cements and pure FA and GGBFS as well. Since the pore water becomes very alkaline when cement is part of the paste, the samples for pure FA and GGBFS have been tested in distilled water with pH 7 and artificial pore water (APW) with pH ~13. This allows us to see whether the pH has an effect on consumption in the mineral admixtures, also simulating the environment the mineral admixtures would have in a cement paste. The APW was prepared by mixing 2.11 g NaOH and 5.93 g KOH per liter distilled water. According to Vikan (2005)<sup>[4]</sup>, this results in a pH of about 13.

As reported, the addition time of SP influences the consumption behavior, so both immediate addition and delayed addition of 10 minutes of LSs are tested. The pH of the paste is also shown to affect the consumption. In order to investigate this effect, pH measurements of the pore water from the pastes have been taken.

The LSs consumption is to be found through experimental work using UV-spectroscopy analysis. UV-spectroscopy analysis is a technique that can determine the concentration of a

given material in an aqueous solution. Since it is impossible to directly determine the amount consumed LSs in a paste, the pore water containing the non-consumed LSs can be extracted a certain time after mixing and analyzed in an UV-spectrometer to determine the remaining concentration. From this, the amount consumed LSs can be calculated as the difference between the added amount and remaining amount. This experimental method cannot differ between surface-adsorbed and intercalated superplasticizers. The UV-spectrometer scans the solution at a chosen wavelength according to the analyzed material. LSs was scanned for all wavelengths between 190 nm and 1100 nm in distilled water as a blank reference sample. The most apparent peak was found at 281 nm, so this was chosen as the most appropriate wavelength for the LS used. The experimental method used to prepare the pastes is according to the method used by Vikan <sup>[4]</sup>.

### **3.2.1 Mixing procedure**

The following procedure was used in the same manner for all the samples. The chosen addition time of 10 minutes for DA was found to be sufficient for consumption measurements <sup>[10-12]</sup>.

- For *immediate* addition the water, LSs and cement were mixed, then stirred with a Braun MR530 electric hand blender on speed 6 for 30 sec. The paste was homogenized with a spoon and left to rest for 5 minutes before being stirred again on speed 6 for 60 sec.
- For *delayed* addition the cement and 85% of the water were mixed, then stirred with the electric hand blender on speed 6 for 30 sec. The paste was homogenized with a spoon, left to rest for 10 minutes before the addition of LSs and 15% of the water, then stirred again on speed 6 for 60 sec.
- About 40 ml of paste was then placed in 50 ml centrifuge tubes and left to rest until 30 minutes after wetting.
- The pore water was then tested in a Metrohm 6.0225.100 Profitrode pH meter. Before analyzing a sample in a UV-spectroscopy, the sample

### 3.2.2 Pore water analysis

30 minutes after wetting, the paste samples were centrifuged in a Thermo Scientific Heraeus Megafuge 8 centrifuge at 4500 rpm for 3 minutes to extract the pore water. After centrifugation, the pore water was separated and filtrated through a 0.45  $\mu\text{m}$  filter. This ensure that the solution was depleted of cement particles. 1 ml of the pore water was diluted 100 times before it can be scanned in the UV-spectrometer. The UV-spectrometer used was Thermo Scientific Genesys 10S UV-VIS.

### 3.2.3 Measurement of pH

A volume of 2-3 ml of the filtrated pore water was used to measure the pH. The pH meter used was Metrohm 6.0225.100 Profitrode.

### 3.2.4 Analysis of consumed amount LSs

The UV-spectroscopy method provides the intensity as a function on wavelength, called absorbance number, which should be nearly linearly dependent of the concentration of the material in the analyzed sample. There is a near-linear correlation between the absorbance number and concentration of the material. Thus, the absorbance numbers obtained for the unknown concentrations of LSs in paste samples can be compared to absorbance numbers obtained for prepared samples of known concentrations LSs in distilled water. The prepared samples of known concentrations LSs in distilled water were made with concentrations of 0.25, 0.5, 1 and 3 g LSs / 100 g distilled water, then diluted 100 times. The absorbance numbers were then plotted as a function of added LSs using the least square method. These graphs are called *calibration curves*. With these calibration curves, one can calculate the unknown concentration of non-consumed LSs from the paste samples using the obtained corresponding absorbance numbers. The formula for a calibration curve can be expressed as in Eq. 3.1, where  $y$  is the absorbance number,  $x$  is the concentration material in the solution and  $a$  and  $b$  are constants for the material.

$$y = a \cdot x + b \tag{3.1}$$

Eq. 3.2 of the calibration curve for LSs in distilled water is found using the least square method on the absorbance numbers in Table A.1. The calibration curve is plotted in Fig. 3.1.

$$y = 0.888x + 0.063 \quad (3.2)$$

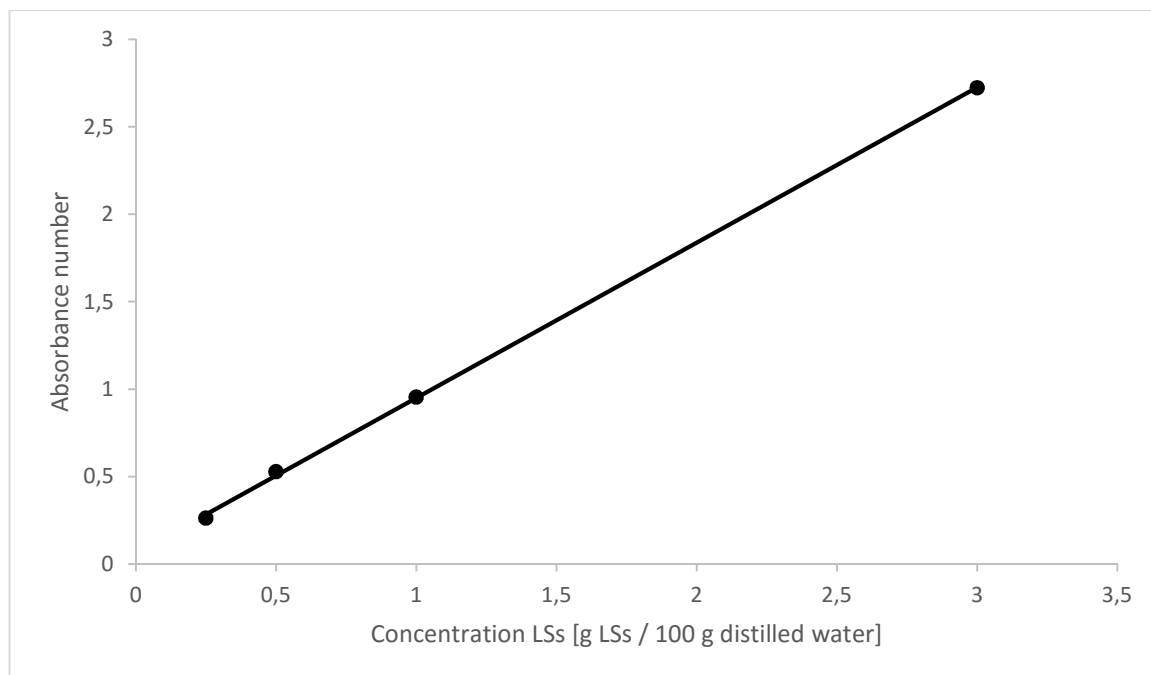


Fig. 3.1. Calibration curve for LSs in distilled water.

When analyzing LSs consumption in paste samples with APW, the calibration curves must reflect the use of APW. LSs samples in APW were therefore prepared with concentrations of 0.25, 0.5, 1 and 3 g LSs / 100 g APW. These samples were diluted 100 times; both dilution with distilled water and with APW were tested to see which of the calibration curves was most fit for the experiment.

Eq. 3.3 of the calibration curve for LSs in APW diluted 100 times in distilled water and Eq. 3.4 of the calibration curve for LSs in APW diluted 100 times in APW are found using the least square method on the results in Table A.1 For the calibration curve diluted 100 times in APW, only the three lowest absorbance numbers are used, since the highest value does not follow the linear correlation. The calibration curves are plotted in Fig. 3.2.

$$y = 1.001x + 0.026 \quad (3.3)$$

$$y = 1.041x + 0.029 \quad (3.4)$$

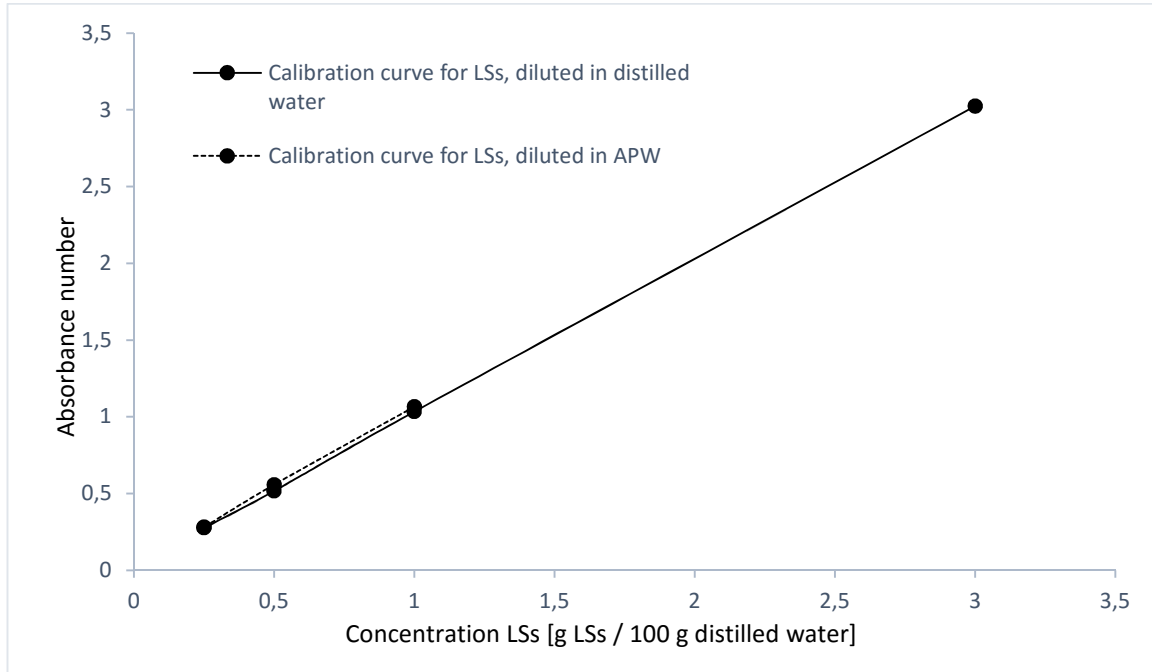


Fig. 3.2. Calibration curve for LSs in APW.

Using the calibration curves, where the constants  $a$  and  $b$  are known (Eq. 3.1), one can calculate the concentration LSs in the analyzed pore water. Eq. 3.1 can be reformulated to Eq. 3.5, which gives the concentration  $C$  of the non-consumed LSs [g LSs / 100 g pore water] as a function of the absorbance number  $abs$  and the given constants  $a$  and  $b$ :

$$C = \frac{abs - b}{a} \quad (3.5)$$

However, this only gives the concentration in the water phase. The concentration of LSs is given as weight LSs per weight binder. Multiplying the concentration  $C$  by the  $w/b$ -ratio results the non-consumed amount g LSs per 100 g binders. Subtracting this from the initially added amount of LSs gives the amount consumed in grams LSs per 100 g binders:

$$Consumed\ LSs = Added\ LSs - C \cdot \frac{w}{b} \quad (3.6)$$

The consumed amount LSs per surface area of binders was also calculated. The BET surface area differs between the four materials (see Table 3.3), so calculation of the surface area for all blended cements was necessary. The consumed amount LSs per weight (Eq. 3.6) was then divided by the specific surface area for each of the blended cement samples to obtain values for the consumed amount LSs per surface area.

Some of the higher LSs values were not measurable using this experimental method. Table 3.5 lists all LSs values that were successfully analyzed.

### 3.2.5 Consumption as a function of hydration time

As part of planning the experimental part, knowledge about how the hydration time before extracting pore water affect the consumption levels is needed. A series of tests were performed to find the consumption as a function of hydration time for neat ANL and CX. The consumed amount LSs with initial concentration of 0.4 wt% was measured for both ANL and CX after 10, 30, 60, 120 and 180 minutes. As seen in Fig. 3.3, it is apparent that the consumption process continues even after 30 minutes, as chosen in this experimental plan. The numerical values are listed in Table A.21.

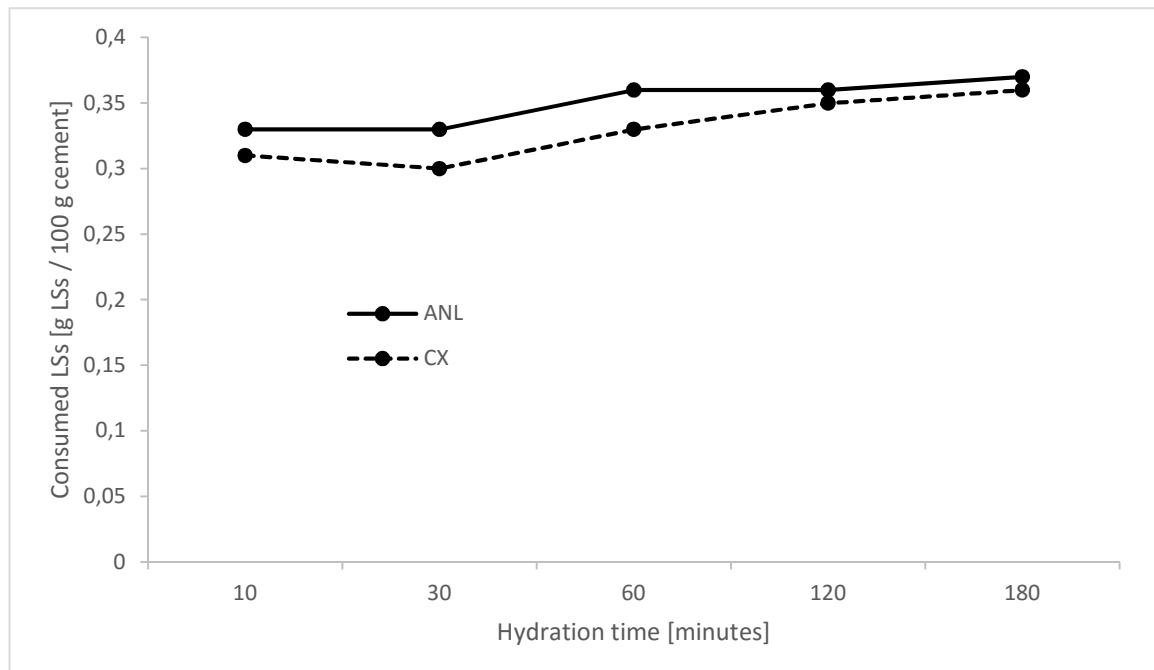


Fig. 3.3. LSs consumption in neat ANL and CX as a function of hydration time. 0.4 g LSs / 100 g cement was added.

### 3.2.6 Accuracy

In order to demonstrate the accuracy of the experimental results, some experiments have been repeated three times. These test series indicate the standard deviation of the results from three repeated experiments for the same tests. For adsorption isotherms, the values 0.1, 0.4 and 1.2 g LSs / 100 g binder have been repeated three times for all blended cement samples. For pH measurements, the values 0 and 0.8 g LSs / 100 g binder have been repeated three times for the neat cements.

The standard deviation,  $s_x$ , is calculated

$$s_x = \sqrt{\frac{1}{1-n} [(x_1 - x_{AV})^2 + (x_2 - x_{AV})^2 + \dots + (x_n - x_{AV})^2]} \quad (3.7)$$

where

- $n$  is the number of repeated experiments within the chosen data point
- $x$  is the consumed amount LSs
- $x_{AV}$  is the average consumed amount LSs within the chosen data point

Since the experiments have been repeated three times ( $n=3$ ), Eq. 3.7 reduces to

$$s_x = \sqrt{\frac{1}{2} [(x_1 - x_{AV})^2 + (x_2 - x_{AV})^2 + (x_3 - x_{AV})^2]} \quad (3.8)$$

Table 3.5 – List over tested LSs values for adsorption isotherms and pH measurements.

Material	LSs addition procedure	LSs dosage tested [g LSs / 100 g binder]	
		Adsorption isotherm	pH measurement
ANL cement	IA	0.1; 0.2; 0.4; 0.8; 1.2; 1.5	0.0; 0.4; 0.8
	DA	0.05; 0.1; 0.2; 0.4; 0.8; 1.2; 1.5	0.4; 0.8
CX cement	IA	0.1; 0.2; 0.4; 0.8; 1.2; 1.5	0.0; 0.4; 0.8
	DA	0.05; 0.1; 0.2; 0.4; 0.8; 1.2; 1.5	0.4; 0.8
ANL cement, 30% FA	IA	0.1; 0.2; 0.4; 0.8; 1.2; 1.5	0.0; 0.4; 0.8
	DA	0.05; 0.1; 0.2; 0.4; 0.8; 1.2	0.4; 0.8
ANL cement, 60% FA	IA	0.1; 0.2; 0.4; 0.8; 1.2; 1.5	0.0; 0.4; 0.8
	DA	0.05; 0.1; 0.2; 0.4; 0.8; 1.2; 1.5	0.4; 0.8
ANL cement, 30% GGBFS	IA	0.1; 0.2; 0.4; 0.8; 1.2; 1.5	0.0; 0.4; 0.8
	DA	0.05; 0.1; 0.2; 0.4; 0.8	0.4; 0.8
ANL cement, 60% GGBFS	IA	0.1; 0.2; 0.4; 0.8; 1.2; 1.5	0.0; 0.4; 0.8
	DA	0.05; 0.1; 0.2; 0.4; 0.8	0.4; 0.8
CX cement, 30% FA	IA	0.1; 0.2; 0.4; 0.8; 1.2; 1.5	0.0; 0.4; 0.8
	DA	0.05; 0.1; 0.2; 0.4; 0.8; 1.2; 1.5	0.4; 0.8
CX cement, 60% FA	IA	0.1; 0.2; 0.4; 0.8; 1.2; 1.5	0.0; 0.4; 0.8
	DA	0.05; 0.1; 0.2; 0.4; 0.8; 1.2; 1.5	0.4; 0.8
CX cement, 30% GGBFS	IA	0.1; 0.2; 0.4; 0.8; 1.2; 1.5	0.0; 0.4; 0.8
	DA	0.05; 0.1; 0.2; 0.4; 0.8; 1.2; 1.5	0.4; 0.8
CX cement, 60% GGBFS	IA	0.1; 0.2; 0.4; 0.8; 1.2; 1.5	0.0; 0.4; 0.8
	DA	0.05; 0.1; 0.2; 0.4; 0.8; 1.2	0.4; 0.8
Pure FA, distilled water	IA	0.1; 0.2; 0.4; 0.8	0.0; 0.4; 0.8
Pure GGBFS, distilled water	IA	0.1; 0.2; 0.4; 0.8; 1.2; 1.5	0.0; 0.4; 0.8
Pure FA, APW	IA	0.1; 0.2; 0.4; 0.8	0.0; 0.4; 0.8
Pure GGBFS, APW	IA	0.1; 0.2; 0.4; 0.8; 1.2; 1.5	0.0; 0.4; 0.8



# Chapter 4

## Results

### 4.1 Adsorption isotherms

Adsorption isotherms for all measured combinations of cement types and mineral admixtures are given in Fig. 4.1 – Fig. 4.6, with these isotherms showing both IA and DA of LSs. The results are presented both as consumed amount LSs per weight percent of binder and per BET surface area in  $\text{m}^2$  for unhydrated binder. The raw data used for calculation and the numerical values of the isotherms are given in Appendix A. Some higher concentrations were not analyzed since the pore water at these concentrations could not be extracted.

The six adsorption isotherms presented depict the dependence on the various parameters of LSs consumption and makes clear whether a plateau is apparent at higher concentrations of LSs. Repeated test series were completed to find standard deviations for cement blended with mineral admixtures only.

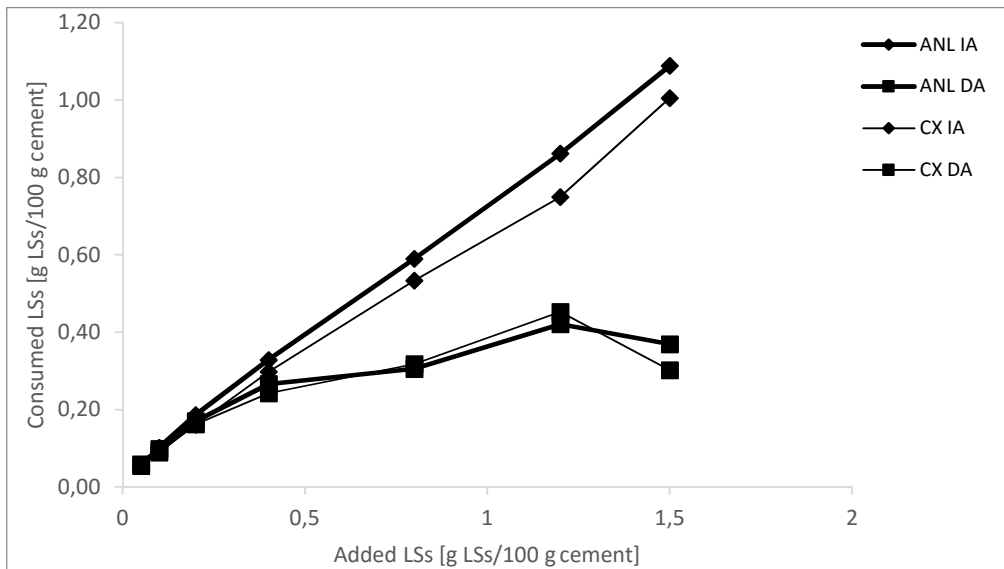


Fig. 4.1. Amount of consumed LSs vs. added amount LSs in neat ANL and CX for IA and DA after 30 min. hydration. The values are calculated as mass% of LSs divided by the mass% of cement.

As for neat cements (Fig. 4.1), IA of both ANL and CX shows no signs of a plateau or decline in percentage consumed amount LSs due to its linear form. In this case, neat ANL seem to have higher consumption than neat CX. For the case of DA, signs of a plateau are apparent after concentration of 0.4 g LSs/100 g binders. The difference between the two cement types is small for DA.

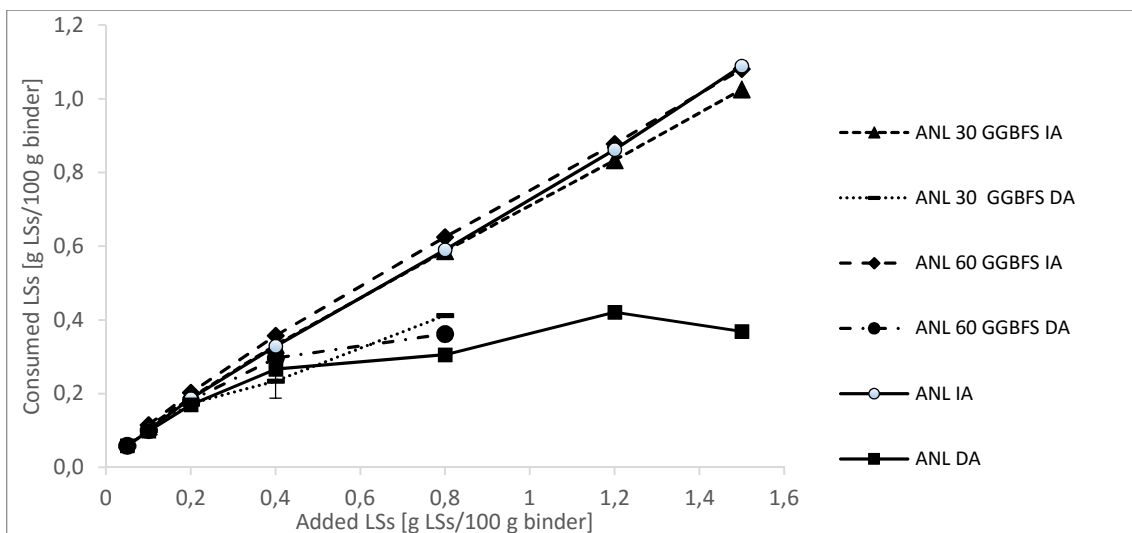


Fig. 4.2. Amount of consumed LSs vs. added amount LSs in ANL with addition of GGBFS for IA and DA after 30 min. hydration. The values are calculated as mass% of LSs divided by the mass% of binders. GGBFS blended ANL cement for DA was not measurable for 1.2 and 1.5 g LSs/100 g binder.

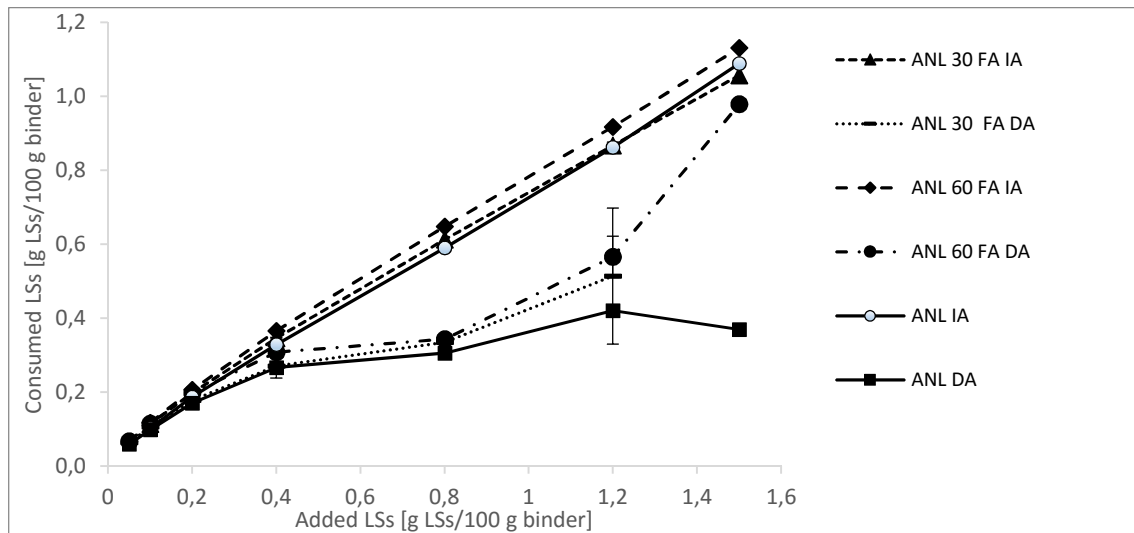


Fig. 4.3. Amount of consumed LSs vs. added amount LSs in ANL with addition of FA for IA and DA after 30 min. hydration. The values are calculated as mass% of LSs divided by the mass% of binders. FA blended ANL cement for DA with 60% replacement level was not measurable for 1.5 g LSs/100 g binder.

Fig. 4.2 and Fig. 4.3 show the adsorption isotherms for ANL cement with mineral admixtures. The contribution in consumption of LSs between FA and GGBFS in ANL is small. Especially for IA, the blended cements seem to behave the same way as neat cements. For DA, the consumption seems to be higher for blended cements, however this difference is within the error. In most cases, the consumption was higher for 60% replacement than 30% replacement. Within the span of concentrations added LSs tested, i.e. up to 1.5 g LSs / 100 g binder, no signs of a plateau are apparent. A very large standard deviation was found for higher values of added LSs for DA in Fig. 4.3. This means that the significance of the higher values is reduced. For 60% FA replacement with DA, the consumption values increase again after an indication of a plateau.

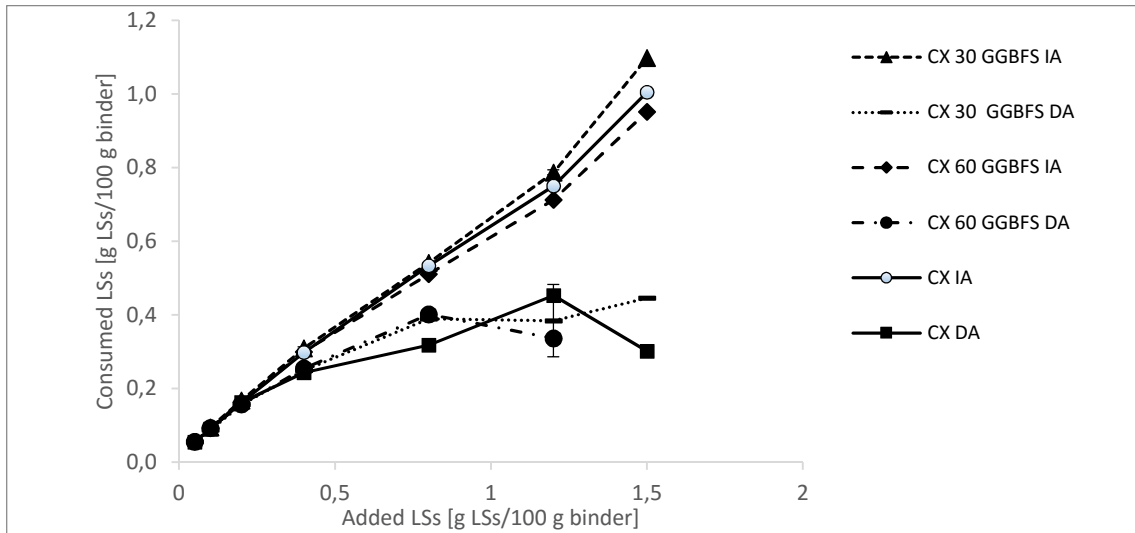


Fig. 4.4. Amount of consumed LSs vs. added amount LSs in CX with addition of GGBFS for IA and DA after 30 min. hydration. The values are calculated as mass% of LSs divided by the mass% of binders. GGBFS blended CX cement for DA with 60% replacement level was not measurable for 1.5 g LSs/100 g binder.

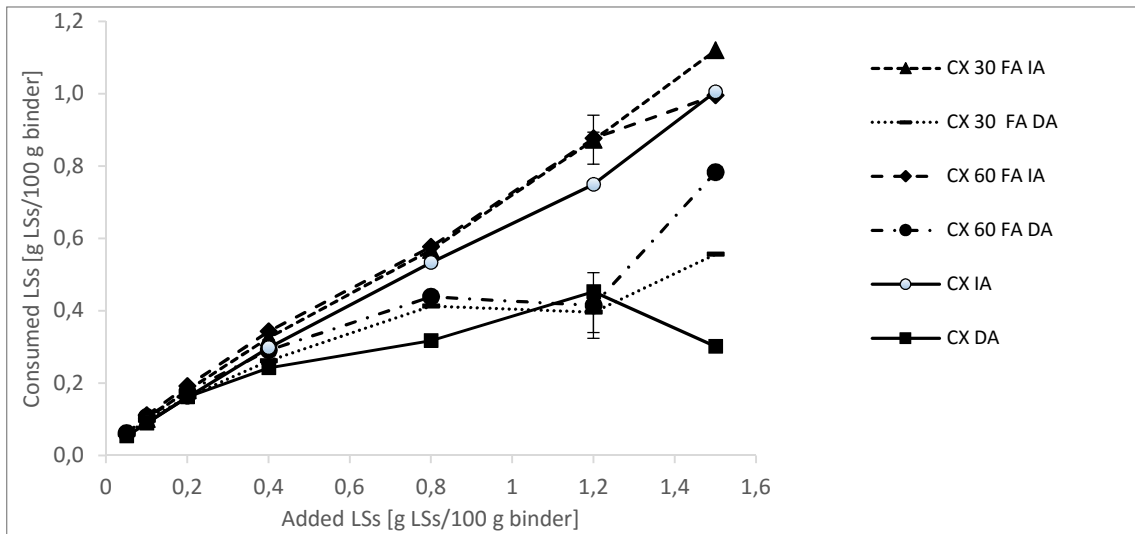


Fig. 4.5. Amount of consumed LSs vs. added amount LSs in CX with addition of FA for IA and DA after 30 min. hydration. The values are calculated as mass% of LSs divided by the mass% of binders.

Fig. 4.4 and Fig. 4.5 show the adsorption isotherms for CX cement with mineral admixtures. It is clear that the differences between FA replacement and GGBFS replacement are larger for CX cement than ANL cement. FA blended CX cement seem to consume more LSs than neat CX, however these differences are also within the error. For FA blended CX cement using DA, the consumption values increase again after an indication of a plateau. GGBFS blended CX cement had only small differences compared to the neat CX cement. A plateau is detectable in the isotherms for DA after 0.8 g LSs / 100

g binder for replacements of FA and GGBFS. For IA no plateau is as apparent.

For all isotherms, the consumption of LSs is much larger for IA than DA for higher values added LSs. This difference increases with higher concentration added LSs.

## **4.2 Adsorption isotherms in APW for pure FA and GGBFS**

For pure FA and GGBFS, adsorption isotherms are found for IA only. To investigate whether the pH in the samples would affect the interaction between the mineral admixtures and LSs, the samples were prepared with distilled water with pH 7 and APW with pH 13 to simulate the environment of a cement paste. The results from LSs in APW were analyzed using the three different calibration curves, Eq. 3.2, Eq. 3.3 and Eq. 3.4, to see which one is the most suitable for calculating the consumed amount LSs. For the adsorption isotherm for pure FA and GGBFS in distilled water, only the calibration curve in Eq. 3.2 is used.

Surprisingly, most of the calculated values of LSs consumption in pure FA and GGBFS in APW were negative, irrespectively of which of the calibration curves was used. The absorbance numbers obtained for pure FA and GGBFS in APW, Table A.7, were high enough that the calculated amount for consumption was negative. When the pore water for pure FA in APW was extracted, it was observed that this pore water was much darker than pore water from other samples, even after filtrating. The dark color observed matches the color of the used FA. The results are shown in Fig. 4.6 for pure FA and GGBFS in distilled water. The adsorption isotherms for pure FA and GGBFS in APW using calibration curve in Eq. 3.2 are also in Fig. 4.6.

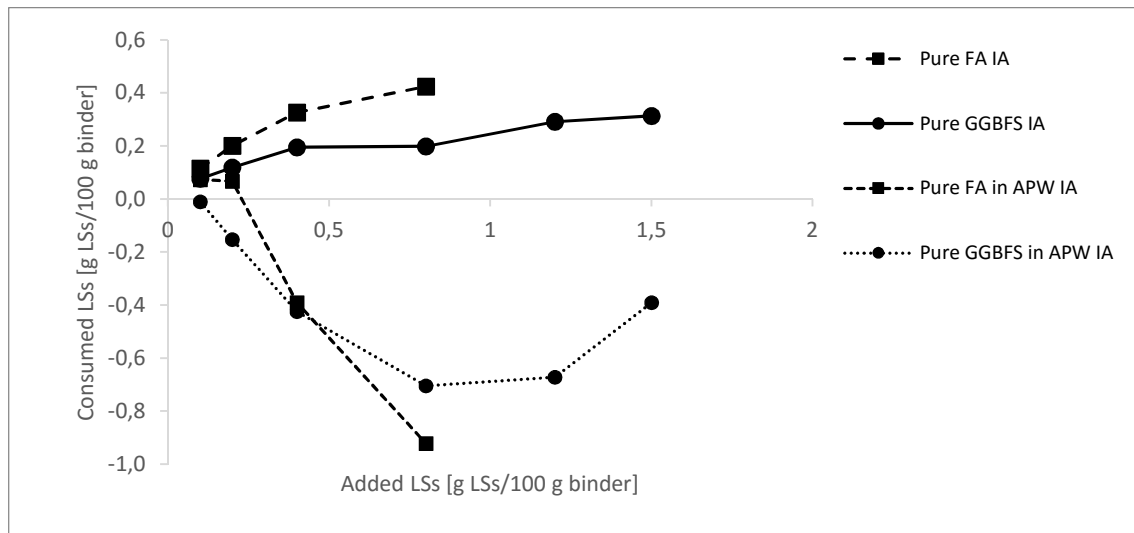


Fig. 4.6. Amount of consumed LSs vs. added amount LSs in pure FA and GGBFS for IA in distilled water with pH 7 and in APW with pH 13 after 30 min. The values are calculated as mass% of LSs divided by the mass% of binders. Pure FA in distilled water and APW was not measurable for 1.2 and 1.5 g LSs/100 g binder.

It is apparent that FA has a higher consumption of LSs than GGBFS, and this difference increase with increasing concentration added LSs. While a plateau is not clearly evident in Fig. 4.6, there are signs of a decline in consumption with increasing concentration added LSs for the span of concentrations tested.

### 4.3 Adsorption isotherms based on surface area

Adsorption isotherms are usually presented in term of consumption per weight of binders. However, the interface between the adsorbate and the adsorbent in this study is on the surface of the binders. It is therefore interesting to depict adsorption isotherms based on surface area to compare with the isotherms already presented in Chapter 4.1.

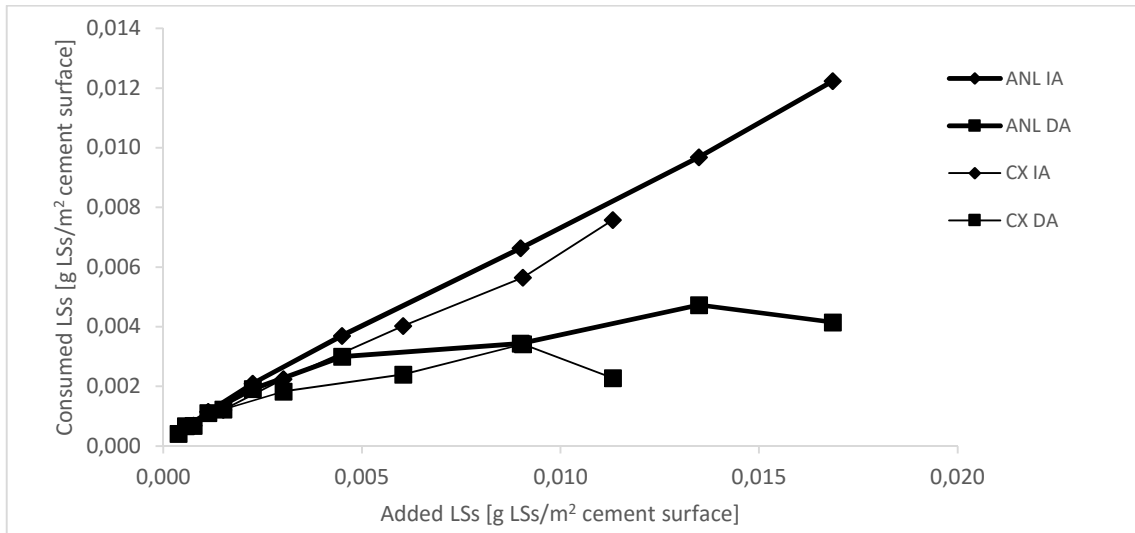


Fig. 4.7. Amount of consumed LSs vs. added amount LSs in neat ANL and CX for IA and DA after 30 min. hydration. The values are calculated as mass% of LSs divided by the BET surface area of cements

When comparing the consumption in neat cements between the two isotherms, Fig. 4.1 and Fig. 4.7, it is apparent that the difference between ANL and CX for DA increases when studying the latter isotherm. As seen in both isotherms, ANL still has a higher LSs consumption than CX.

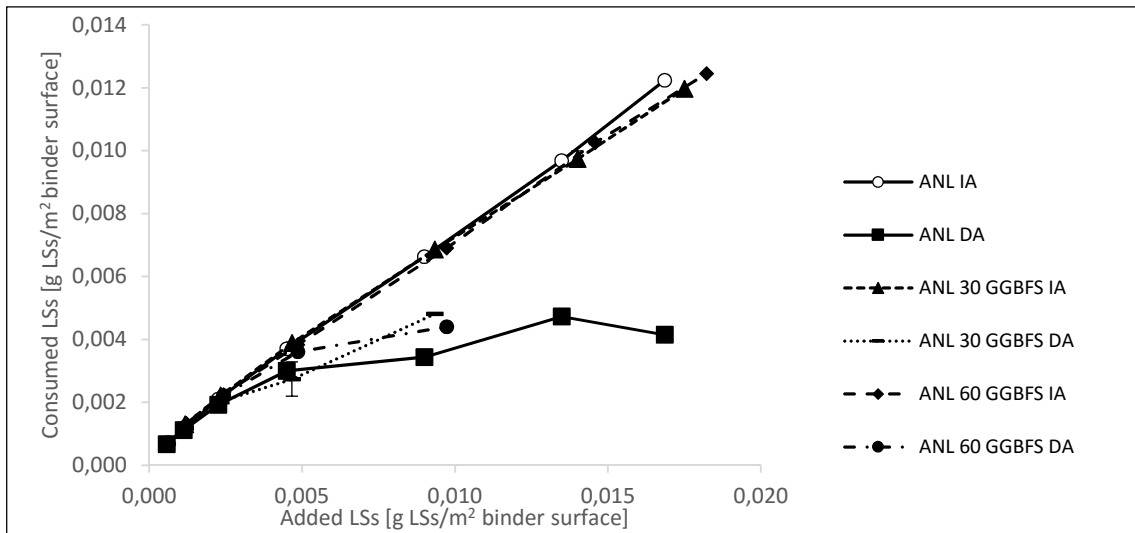


Fig. 4.8. Amount of consumed LSs vs. added amount LSs in ANL with addition of GGBFS for IA and DA after 30 min. hydration. The values are calculated as mass% of LSs divided by the BET surface area of binders. GGBFS blended ANL cement for DA was not measurable for 1.2 and 1.5 g LSs/100 g binder.

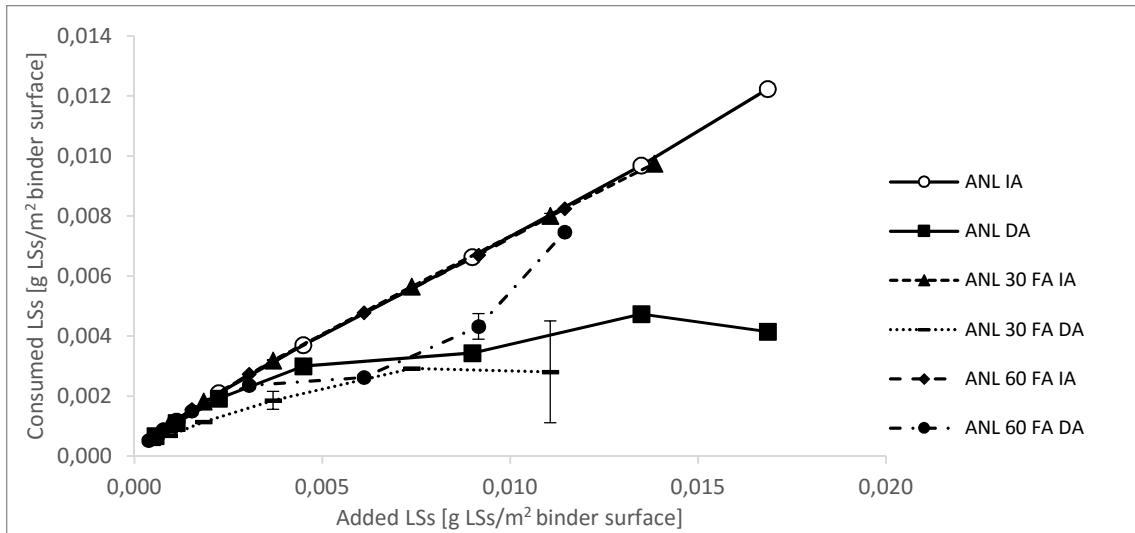


Fig. 4.9. Amount of consumed LSs vs. added amount LSs in ANL with addition of FA for IA and DA after 30 min. hydration. The values are calculated as mass% of LSs divided by the BET surface area of binders. FA blended ANL cement for DA with 60% replacement level was not measurable for 1.5 g LSs/100 g binder.

In Fig. 4.2 and Fig. 4.8 the isotherms for ANL with addition of GGBFS are given. There is little difference between the two isotherms since the BET surface area of ANL and GGBFS are comparable. However, FA has a significantly higher BET surface area than ANL. Thus, for the isotherm based on surface area, Fig. 4.9, the consumption is reduced when FA is used as a binder, for both 30% and 60% replacement. This is more readily apparent for DA than for IA. However, large standard deviations are present, so the significance of this difference can be discussed.

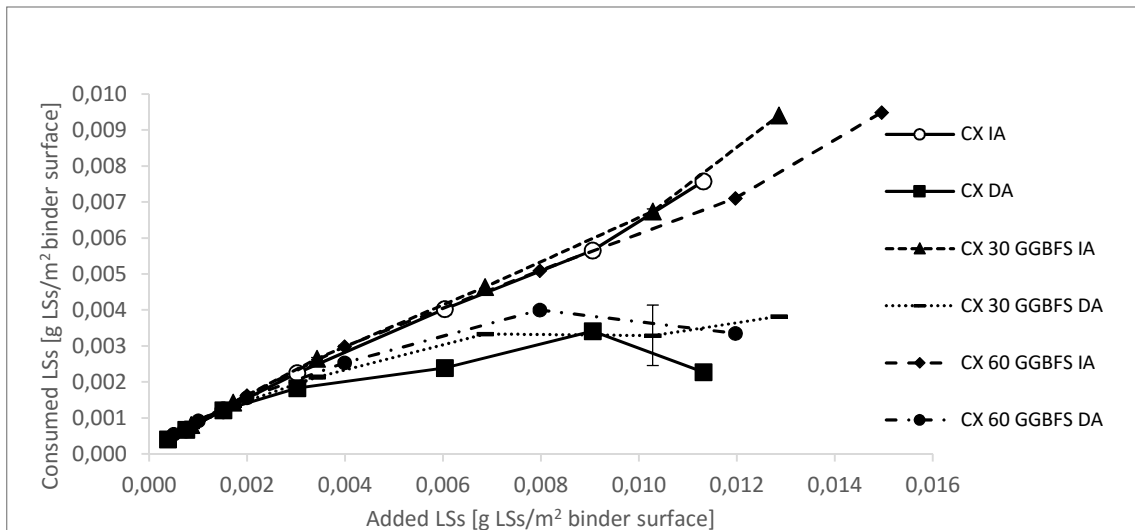


Fig. 4.10. Amount of consumed LSs vs. added amount LSs in CX with addition of GGBFS for IA and DA after 30 min. hydration. The values are calculated as mass% of LSs divided by the BET surface area of binders. GGBFS blended CX cement for DA with 60% replacement level was not measurable for 1.5 g LSs/100 g binder.



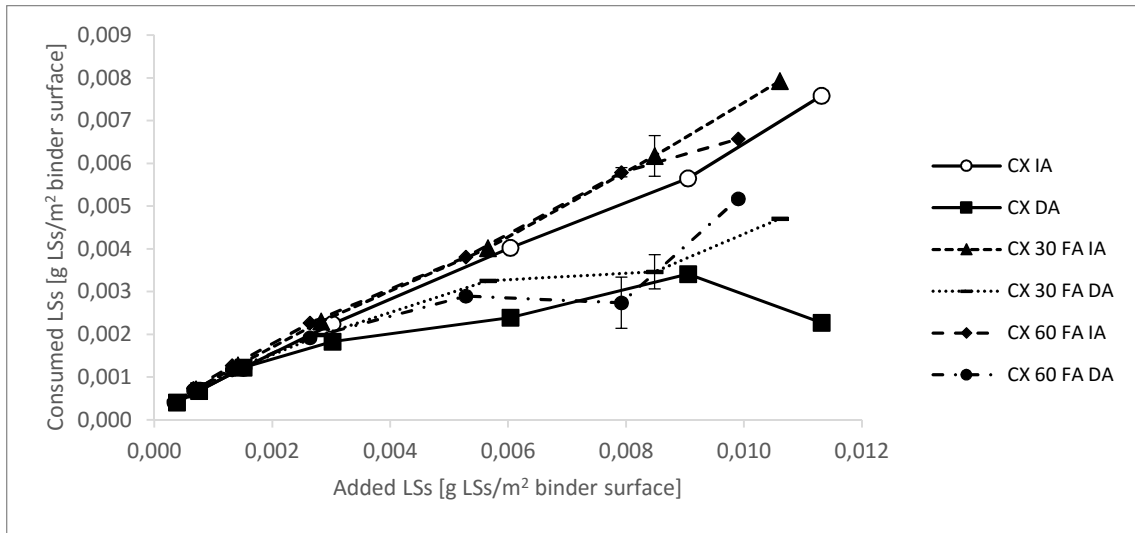


Fig. 4.11. Amount of consumed LSs vs. added amount LSs in CX with addition of FA for IA and DA after 30 min. hydration. The values are calculated as mass% of LSs divided by the BET surface area of binders

Since CX is a finer material than GGBFS, the consumption per surface area increases with increasing replacement with GGBFS, Fig. 4.10. This difference is especially visible for DA, where the difference in consumption per weight is also greatest between replacement levels. The BET surface area is more comparable between CX and FA, meaning that isotherms, Fig. 4.5 and Fig. 4.11, are more similar as well.

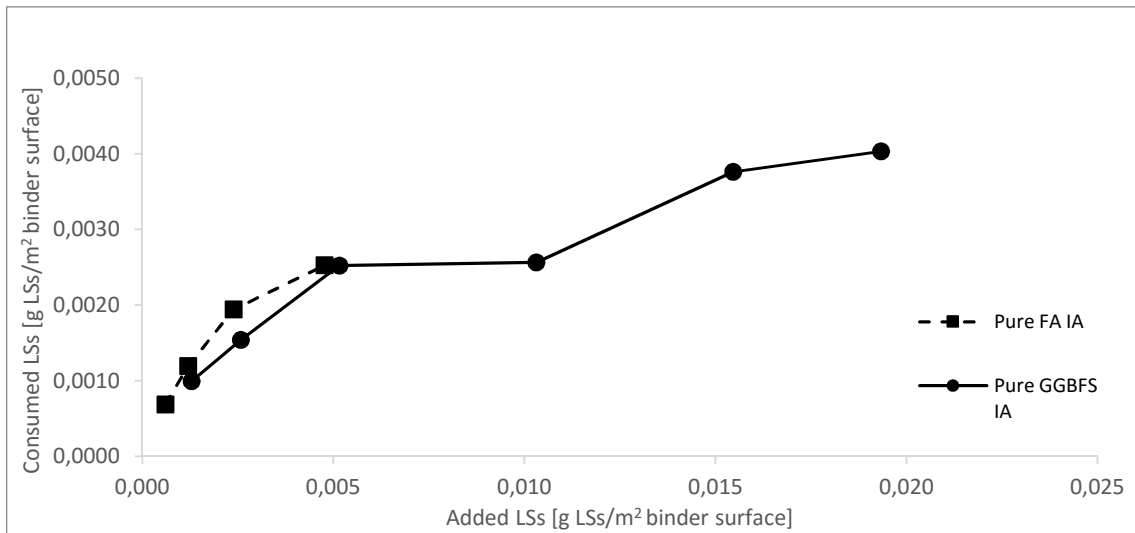


Fig. 4.12. Amount of consumed LSs vs. added amount LSs in pure FA and GGBFS for IA in distilled water with pH 7 and in APW with pH 13 after 30 min. The values are calculated as mass% of LSs divided by the BET surface area of binders. Pure FA in distilled water and APW was not measurable for 1.2 and 1.5 g LSs/100 g binder.

The consumption amount for pure FA and GGBFS is more similar when comparing consumption per surface area, Fig. 4.12, than consumption per binder weight, Fig. 4.6.

## 4.4 pH measurements

pH values for 30 minutes hydrated paste samples of ANL and CX with and without replacement of FA and GGBFS are presented for IA and DA. LSs was added in levels of 0.4 and 0.8 g LSs / 100 g binder. Paste samples were also tested without addition of LSs.

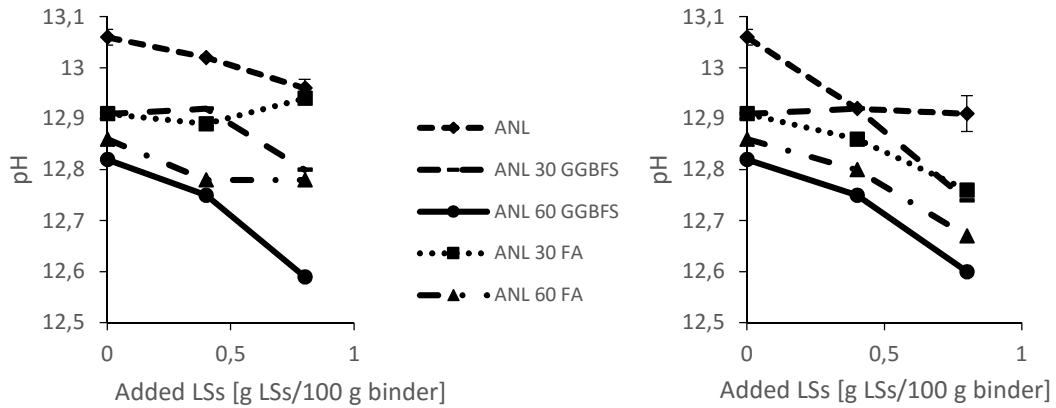


Fig. 4.13 (left). pH values for blended ANL cement with and without of LSs for immediate addition.

Fig. 4.14 (right). pH values for blended ANL cement with and without of LSs for delayed addition.

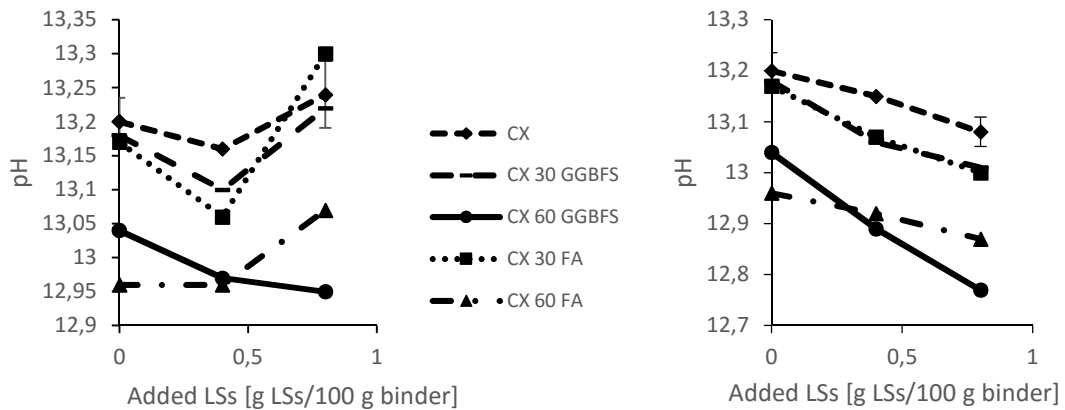


Fig. 4.15 (left). pH values for blended CX cement with and without of LSs for immediate addition.

Fig. 4.16 (right). pH values for blended CX cement with and without of LSs for delayed addition.

Fig. 4.13 - Fig. 4.16 depict the measured pH for all cements with FA and GGBFS for different addition levels of LSs. Several parameters seem to affect the pH of the pastes. First, it is clear that the neat cements have a higher pH than blended cements for most of the samples. The higher replacement level of 60% results in an even lower pH than 30% replacement does. However, it is hard to conclude on which mineral admixture have the greatest impact on the pH of the blended cements, though in Fig. 4.17 it is clear that FA has a lower pH than GGBFS. Also, the addition of LSs reduces the pH of the paste for

most samples except CX IA. Not surprisingly, the use of APW in pure FA and GGBFS increase the pH compared to the use of distilled water.

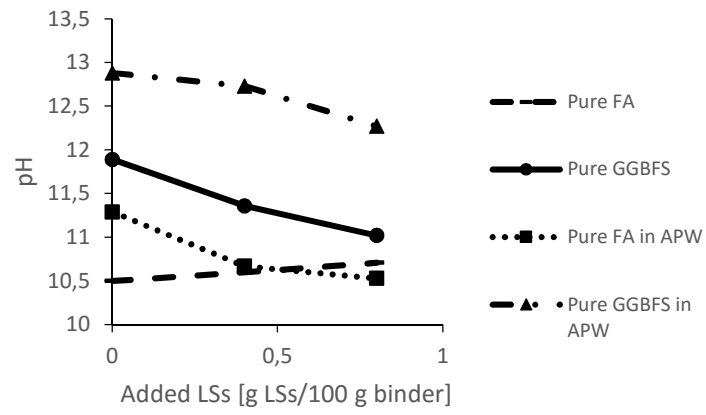


Fig. 4.17. pH values for pure FA and GGBFS with and without of LSs for immediate addition.



# Chapter 5

## Discussion

The objective of this study is to investigate the effects of different parameters on consumption of LSs. There are several mechanisms behind the consumption of LSs and reactivity that can work together. As presented in Chapter 4, the adsorption isotherms differ according to materials and addition methods. This discussion aims to evaluate the reported parameters' effects on LSs consumption, i.e., estimate the significance of the parameters in light of the theories presented in Chapter 2 and the obtained adsorption isotherms. Although the subject of SP consumption is much discussed in the literature, a great deal of discussion and uncertainty about certain parts of the subject remains.

### 5.1 Effects of FA and GGBFS on LSs consumption

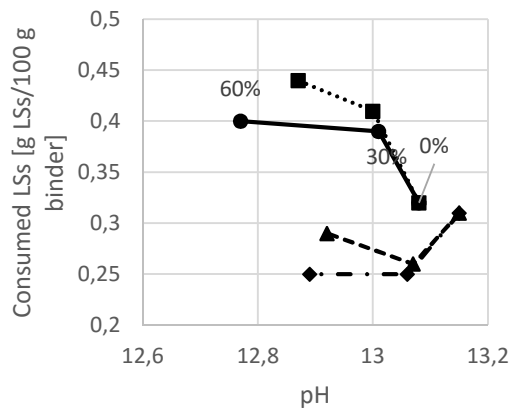
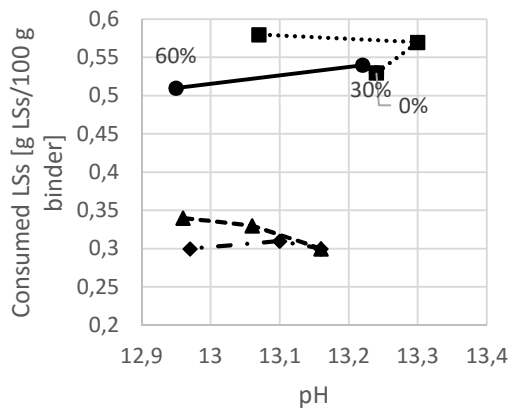
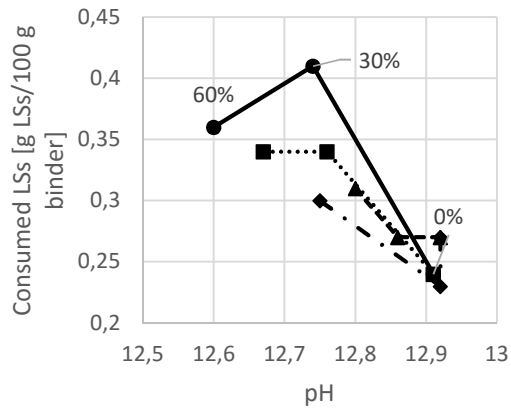
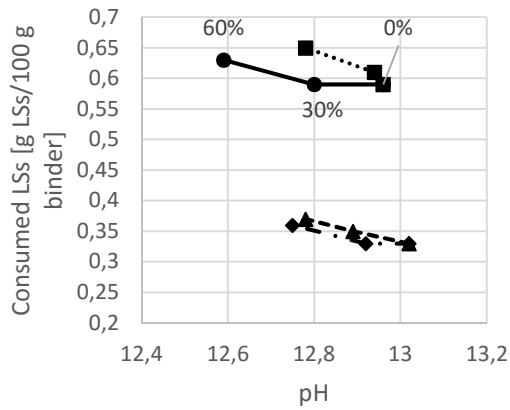
Replacing a part of OPC with FA or GGBFS changes the chemical composition of the paste. As a result, the reactivity between SP and binders is expected to change. Fig. 4.6 shows the consumption on pure FA and GGBFS. It is clear that pure FA has a much higher capacity to consume LSs than pure GGBFS does. However, as seen in the adsorption isotherms based on weight, Fig. 4.2 – Fig. 4.5, the difference between cements blended with FA and cements blended with GGBFS are small. For many of the isotherms using DA, it seems that blended cements have higher consumption than neat cements. However, the standard deviations of the same isotherms are often larger than the differences in consumption between the materials. With such high standard deviations, it is impossible to conclude the significance of these differences. The standard deviation tends to increase with increasing concentrations LSs for most isotherms.

For the adsorption isotherms based on surface area, Fig. 4.7 – Fig. 4.11, some of the

differences seems to increase, especially for DA. Even though the differences increase for some isotherms when based on surface area, the significance of these differences is uncertain, since the standard deviations are quite high. Moreover, it was reported that pure FA consumes more than pure GGBFS. Taking the BET surface area into account, the consumption of LSs between the two materials is much more similar. FA has about twice the surface area of GGBFS. The LSs consumption in the isotherm based on weight in Fig. 4.6 shows about twice as much consumption in FA compared to GGBFS; but for the isotherm based on surface area, the consumption interestingly become comparable. It seems more plausible that the differences between consumption on pure FA and pure GGBFS can be contributed to the difference in surface *area* rather than differences in surface *reactivity*.

## 5.2 Influence of the pH

Increased pH has been shown to decrease the consumption of LS <sup>[6, 14]</sup>. This is reported to be a result of poly-electrolytic expansion of the polymers on the surface sites. Using binders with lower pH therefore contributes to increased consumption. The use of FA and GGBFS has been shown to reduce the pH of both ANL and CX (Chapter 4.4), where the highest replacement level results in the largest decrease in all samples. The correlation between pH and consumption are evaluated in this study. Fig. 5.1 – Fig. 5.4 shows the consumption as a function of pH for blended and neat cements. The three replacement levels 0%, 30% and 60% goes from left to right in the graphs.



-◆- 0.4 GGBFS    -▲- 0.4 FA  
 -●- 0.8 GGBFS    -■- 0.8 FA

Fig. 5.1 (upper left). pH values and consumption levels for ANL cements with IA.

Fig. 5.2 (upper right). pH values and consumption levels for ANL cements with DA.

Fig. 5.3 (lower left). pH values and consumption levels for CX cements with IA.

Fig. 5.4 (lower right). pH values and consumption levels for CX cements with DA.

As seen in the graphs, no significant trend between lower pH and increased LSs consumption is apparent in this study. It is clear that with higher replacement of FA or GGBFS, the pH decreases, but the consumption level seems not to have any apparent correlation to the pH. The pH range in this study is much smaller than the range used by K. R. Ratinac, so the contribution from the small differences in pH might be insignificant. This might be an explanation of the findings in this study.

### 5.3 Delaying addition

One of the first assumptions in this study was regarding the difference in consumption between IA and DA. Cement reacts with water immediately after wetting, forming hydrates that continuously renew the outer surfaces available for LSs adsorption. Within the first minutes of IA, the surface-adsorbed LSs are intercalated in growing hydrates through the first initial hydration, forming an organo-mineral phase<sup>[9]</sup>. With DA, most of these hydrates have already formed before the addition of LSs, resulting in little intercalation<sup>[4,7, 10-12]</sup>. Since there are more LSs available for a smaller surface area the consumption of the polymer is thought to be smaller than for IA. As seen in Chapter 4, the hypothesis is consistent with the adsorption isotherms for high concentrations of added LSs. At high LSs concentrations, IA has more than twice the consumption than DA; however, at low concentrations, the difference is not significant.

The effect of delaying addition of the polymer increases with higher concentrations. This can be explained with the model presented by Flatt & Houst (2001)<sup>[9]</sup>. According to this model, SP added to a paste is either adsorbed on the surface of particles, intercalated inside hydrates or free in the aqueous solution. As mentioned, after 10 minutes of hydration, most of the early hydrates are formed. Even though IA consumes more of the polymers, the fluidity of a paste improves with DA compared to IA since the intercalated amount of LSs has little to no effect on workability<sup>[9]</sup>. This effect on rheology was detected during the experimental program; using DA of LSs increased the fluidity to a large degree.

Another effect to be considered when comparing the results from IA and DA is the replacement levels of GGBFS and FA. Since the *early* hydrates are mostly a product of *cement* hydration only<sup>[42]</sup>, little effect should be achieved when delaying addition in a cement with high replacement levels of FA or GGBFS compared to IA. One can assume that, if FA and GGBFS do not contribute significantly to the formation of *early* hydrates, the difference between IA and DA becomes smaller with increasing replacement levels of mineral admixtures. The results show that this is true to some extent for FA replacement of both ANL and CX, though this difference is not noticeably for GGBFS replacement. The significance of this difference is not certain, since the standard deviation is quite high for these values. If FA naturally consumes more LSs than GGBFS, this difference could be expected. As seen in Fig. 4.6, FA has about twice the consumption capacity as GGBFS, though this difference is reduced when comparing consumption per surface area in Fig.



4.12. However, some chemical activity from the mineral admixtures is to be expected after wetting a blended cement. Since the measured pH in pure FA and GGBFS samples, Fig. 4.17, varies from that of distilled water and APW, some chemical activity appears to occur a short time after wetting. From this it can be argued that the early hydrates formed or the early reactivity in the paste may be perturbed by the mineral admixtures. This might happen because the mineral admixtures consume a lesser amount of LSs than the cement, resulting in a higher polymer/cement ratio, which is again shown to alter the formation of early hydrates<sup>[43]</sup>, or the fact that the reactivities of all components in a paste change when adding an active material.

## 5.4 Chemical composition of cement

One of the mechanisms behind consumption is intercalation, which is thought to be most dominant in cements containing large amounts  $C_3A$  and  $C_4AF$ <sup>[4, 5, 15]</sup>. This is because the growth of early hydrates such as ettringite, one of the AFt phases, mainly comes from these phases. The early hydrates are responsible for the LSs intercalation detected in this study. A cement richer in calcium silicate phases will have a slower initial hydration after wetting, so this phenomenon should not be as visible. Björnström & Chandra (2003)<sup>[13]</sup> also formulate another important parameter regarding early hydrates. They speculate that, in addition to the aluminate content, the  $C_3S/C_2S$  relationship also changes the consumption. The higher this relationship, the higher the degree of hydration.

Contradictory to the hypothesis, it is clear from the adsorption isotherms that, especially for IA, it is in fact ANL that has the highest consumption even though the aluminate content is much higher in CX. At DA this difference is not significant, which could mean that early hydrates accounts for the difference between the two cements consumption ability on LSs. Several explanations are possible. Firstly, the aluminate content in CX was about 5% greater than in ANL. Although this is a significant difference, it could be other forces controlling the consumption more than this difference in  $C_3A$  levels, as in the findings of Björnström & Chandra. Since the  $C_3S/C_2S$  relationship is much higher for ANL than CX, it might be a case where this factor influences the early hydrates in terms of consumption comparable to the influence from aluminate content. Secondly, it might also mean that intercalation in ettringite is not the main part of LSs consumption since ettringite is most produced as  $C_3A$  hydrates in water. It is known that the  $C_4AF$ -phase also accounts for a

great deal of early hydrates compared to the calcium silicates. ANL has more than twice the amount of ferrite as CX, so it is hard to conclude the contribution on LSs consumption from the phases based on these isotherms alone. Further research should be done before a substantial theory can be made.

## 5.5 Fineness of binders

Adsorption of LS is thought to occur on the surface of the cement particles. The consumption should therefore be a function of, amongst other factors, the surface area. The usual adsorption isotherm depicting consumed amount LS per weight of the binders could be compared with the isotherm based on LS consumption per binder surface. The densities of the used materials differ much less than the surface areas. The first noticeable change can be seen when comparing the isotherms for pure FA and GGBFS, (Fig. 4.6 and Fig. 4.12). As reported, the adsorption isotherm based on weight does not account for the different surface areas, so there is a quite significant difference in the two isotherms. The difference between neat ANL and neat CX consumption is also increased when the isotherm based on surface area is used. This shows that using just one set of isotherms might not depict all the necessary information for evaluating LS consumption. This difference could also be explained with the fact that LS may penetrate into the interlayers of hydrates [37].

## 5.6 Multilayer adsorption

The formation of hydrates after wetting cement is not the only immediate reaction. When the cement is wetted, the outer layer releases positive ions, leaving a negatively charged surface [13]. Positive ions might also be released from the inside of the cement particles [35] during hydration. Since both LSs and the surface of the cements now have a negative charge, adsorption will likely not occur unless these positive ions bridge between them. As the negatively charged cement particles react with  $\text{Ca}^{2+}$  ions, they gain a positive surface charge, allowing adsorption of LSs [28, 41], see Eq. 2.5 and Eq. 2.6. This might result in multiple layers of LSs adsorbed on the surface, with positive ions between the layers. If the binder material has a defined surface area with sites for adsorption, then the isotherms should reach a plateau after these sites are occupied, unless multilayer adsorption occurs. This should be most apparent for DA, since consumption only has a minor effect.

If multilayer adsorption does not occur, a plateau should be visible in the adsorption isotherm; i.e., the adsorption isotherm can be described by the Langmuir model. This is because the surface-adsorption can stop after the particles are saturated with a monolayer if the calcium ions do not interlay between the polymer layers. As seen in Fig. 4.1 – Fig. 4.6., a plateau or a substantial decline in consumption is most evident in the neat cements and GGBFS blended cements for DA, while for FA blended cements, the consumption seems to increase again after a decline. For IA, little or no decline is visible for any of the isotherms except pure FA and GGBFS. Since FA is a finer material than GGBFS, this result is surprising. However, the difference between GGBFS blended cements and FA blended cements might result from the higher consumption on GGBFS. Since no clear signs of a plateau are visible on cements with IA, it might mean that consumption in early hydrates is the main contributor to uptake of LSs, and a plateau could be visible for higher doses of added LSs than is tested in these experiments. For pure FA and GGBFS with IA, a plateau was clearly evident. Since we assume little surface activity allowing for consumption in early hydrates, it could indicate that on the mineral admixtures monolayer adsorption is the main mechanism. Since a plateau is visible also in DA on cements, it may indicate that monolayer adsorption on the hydrates might account for most of the consumption of LSs.

## 5.7 Consumption at low LSs concentrations

All of the materials have a defined BET surface area that allows for some varying degree of surface-adsorption of LSs. There are also many other ways of LSs consumption in addition to the surface-adsorption on the unhydrated particles, such as the mechanisms discussed in this chapter. All of the materials have at least one layer of adsorption on the surface in addition to consumption and other mechanisms. For all concentrations of added LSs, some of the polymer might form an adsorbed layer on the particle surface immediately after addition, while the rest is either free, consumed, in multilayers etc. The part LSs that is not immediately adsorbed on the surface is small for lower concentrations, and much higher for the higher concentrations. It is mostly this part that is dependent on the various parameters, since these parameters affect consumption in early hydrates, formation of multilayers etc. The part LSs that is surface-adsorbed immediately should be more or less independent of the dosage of added polymer. Even if the amount of initial surface-adsorption varies between the different materials due to fineness and chemical composition

[5, 15], the differences in consumption between the materials should not be large for very low added LSs dosages, that is until one of the materials is saturated with polymers on the surface. After this concentration, the part LSs that is not immediately adsorbed on the surface must be consumed by other mechanisms, which varies widely according to material and technique used.

As seen in the adsorption isotherms, Fig. 4.1 – Fig. 4.6, the different parameters, such as addition time, cement type and mineral admixture, affect the consumption of LSs. However, these differences in consumption clearly increase with increasing added dose of LSs. All of the consumption levels seem to be much more similar for low concentrations of added LSs, especially below the addition level of 0.2 g LSs/100 g binder. The explanation for this could be that for low concentrations of added LSs, most of the polymer is surface-adsorbed immediately after addition regardless of other consumption mechanisms that differ between the materials and addition time. For higher concentrations of added LSs, there are a great deal more polymer that could not adsorb on the now-saturated surface, and this amount is consumed by other mechanisms or still free in the aqueous phase, depending on material and addition time.

## 5.8 Experimental method

An important component of this study is to evaluate not only the consumption mechanisms of LSs, but also the experimental method used. The experimental method used is based on UV-spectroscopy analysis to scan the pore water for the amount of remaining LSs. The standard deviations obtained for blended cements indicate what level of accuracy can be expected from the results obtained through this method.

As seen in the adsorption isotherms, the standard deviations are significant, especially for higher concentrations of added LSs. The error seems to be increasing as the concentration of added LSs increases. When evaluating the coefficient of variation for all standard deviations, Table C.1 – Table C.4, two trends are apparent: for many samples, the coefficient of variation is somewhat constant or increase for increased doses of added LSs, and it is often higher for DA than for IA. This indicates that the experimental method has larger uncertainties for higher values of added LSs and for DA, which was also seen to significantly increase the fluidity of the pastes. In the experimental part, when extracting

the pore water from samples that had a high fluidity, it was apparent that many more particles were floating in the pore water. Even though this pore water was filtrated, some particles might have passed through the filter, as reported with the samples for pure FA in APW in Chapter 4.2. These particles increase the absorbance number, but the contribution from them to the absorbance number can differ between samples. The same contribution to increased absorbance numbers can be seen in the samples with pure FA in APW: the extracted and filtrated pore water was observed to be have a dark color matching the color of FA.

Also apparent when evaluating consumption is that the samples with the lowest amount added LSs (0.05 g LSs / 100 g binder) have a higher amount consumed than added LSs. This also happens with the next addition level, 0.1 g LSs / 100 g binder. The absorbance number for these samples might be too small due to the low concentration of LSs, which gives an unnaturally high consumption value. Since all the samples of 0.05 g LSs / 100 g binder have a consumption larger than 0.05 g LSs / 100 g binder, it is not likely that this is a random error.

For ANL and CX replaced with FA, an indication of a plateau can be seen for DA at 0.5 – 0.8 g LSs / 100 g binder. However, at higher addition levels of LSs the consumption values increase significantly again, especially at 1.5 g LSs / 100 g binder. This is a surprising finding, and might have several explanations. When the pore water was extracted for 1.5 g LSs / 100 g binder for DA, it was dark colored and very hard to filtrate; the color matched that of the binder. Even after filtrating through a 0.45  $\mu\text{m}$  filter, the pore water still had a slightly gray color. It might be possible that some of the binder particles went through the filter. The obtained absorbance number could then be affected by the particles in the pore water, so that the calculated consumption value had increased error as a result of this.

It is therefore reasonable to believe that this experimental method is most accurate when the tested dose LSs is neither too high nor too low. The samples in this study in APW also seem to be unmeasurable using UV-spectroscopy. Other experimental methods can be a better fit when testing samples that have a high or low LSs concentration. For pH measurements, it is hard to conclude that there is a correlation between tested dosage LSs and the standard deviation.

In this study, a hydration time of 30 minutes was chosen. The chosen hydration time will affect the results; as seen in Fig. 3.3, the cements continue to consume some LSs even after 30 minutes. There is no optimal hydration time for this study, as they all differ. This must be considered when comparing the obtained results with results from similar studies.

# Chapter 6

## Conclusions

Based on the findings in this study, the following can be concluded;

- The result in consumption from replacement of 30% and 60% cement with GGBFS and FA is small and within the error for most samples. The overall trend is that blended cements seem to have the same consumption behavior as neat cements. There are some indications that for DA, the replacement with GGBFS or FA *increases* the consumption across the chosen materials. This might be a result of the different particle surfaces and reactivity. However, the standard deviations are high, so the significance of these results can be discussed.
- The consumed amount LSs in this study was not shown to depend on the pH of the paste. The pH-range found is small, and other parameters might have a larger effect on the consumption.
- Although the different phases are known to give different consumption levels of LS, the C<sub>3</sub>A especially is phase thought to be a main contributor to consumption due to the formation of early hydrates which could intercalate surface-adsorbed polymers. This was not evident in the results, which could mean that intercalation in C<sub>3</sub>A hydrates such as ettringite is not the main contributor to LSs consumption, or that other phases like C<sub>4</sub>AF might also play a significant role.
- The differences between IA and DA are much larger than the other parameters' effects on LSs consumption. For the larger values of added LSs, the effect of delaying addition results in less than half the consumption compared to IA for many samples. This is a result of the early hydrates already being formed when delaying addition, reducing the amount of intercalated LSs. For low LSs concentrations, these differences were small.

- The adsorption isotherms based on surface area might be better for comparing the differences between parameters. The isotherms based on weight do not take the fineness into account, which is important to consumption of polymers. Since the weight of binders is not necessarily a main contributor to consumption, both types of isotherms should be studied to gain a broader view of the differences.
- In this study, most of the experimental part was based on UV-spectroscopy analysis of extracted pore water. This method is often used in similar experiments, and have clear advantages. However, as seen in this study, the method has certain limitations; the accuracy seems to decrease with increasing doses LSs and with the use of APW. This is probably a result of fine particles being able to pass through the filter, thus affecting the absorbance number obtained. At lower concentrations the method also seems to give some consumption values higher than the initial concentrations. However, between the lowest and highest concentrations, this method seems to give results that have a smaller error and can be used when finding adsorption isotherms for the given materials.
- Often for a single study, it cannot be claimed that the results hold for all similar studies. Through the experimental program and results, more knowledge about the limitations for these methods have been gained. Further research within the same field could include using other experimental methods; specifically, different methods for filtration should be examined under further research. In this study, it was shown that FA and GGBFS have the same behavior as cements in regard to LSs consumption. However, it is possible that under higher range of LSs concentrations, the blended cements have different consumption properties. Further research could also include testing higher LSs concentrations that are used in this study if a suitable method for higher concentrations are found, reducing the error experienced at these levels.



# Chapter 7

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# Appendix A

## Absorbance numbers and calculated consumption values for LSs

Table A.1 – Absorbance numbers for different concentrations of added LSs [g LSs / 100 g solution] (left column), scanned in Thermo Scientific Genesys 10S UV-VIS at 281 nm

	<b>Absorbance number</b>		
	<b>Distilled water</b>	<b>APW diluted with APW</b>	<b>APW diluted with distilled water</b>
<b>0.25</b>	0.262	0.283	0.277
<b>0.5</b>	0.528	0.559	0.518
<b>1</b>	0.955	1.067	1.035
<b>3</b>	2.724	2.246	3.026

Table A.2 – Absorbance numbers for different concentrations of added LSs [g LSs / 100 g binder] (left column) in neat cements, scanned in Thermo Scientific Genesys 10S UV-VIS at 281 nm

	<b>ANL IA</b>	<b>ANL DA</b>	<b>CX IA</b>	<b>CX DA</b>
<b>0.05</b>		0.042		0.053
<b>0.1</b>	0.058	0.065	0.082	0.085
<b>0.2</b>	0.092	0.128	0.147	0.145
<b>0.4</b>	0.219	0.357	0.285	0.405
<b>0.8</b>	0.525	1.153	0.642	1.113
<b>1.2</b>	0.808	1.781	1.043	1.690
<b>1.5</b>	0.969	2.557	1.140	2.672

Table A.3 – Absorbance numbers for different concentrations of added LSs [g LSs / 100 g binder] (left column) in ANL cement with addition of GGBFS, scanned in Thermo Scientific Genesys 10S UV-VIS at 281 nm

	<b>ANL 30% GGBFS IA</b>	<b>ANL 30% GGBFS DA</b>	<b>ANL 60% GGBFS IA</b>	<b>ANL 60% GGBFS DA</b>
<b>0.05</b>		0.045		0.044
<b>0.1</b>	0.038	0.063	0.043	0.059
<b>0.2</b>	0.086	0.120	0.095	0.101
<b>0.4</b>	0.209	0.421	0.242	0.281
<b>0.8</b>	0.523	0.902	0.554	0.991
<b>1.2</b>	0.855		0.819	
<b>1.5</b>	1.089		1.071	

Table A.4 – Absorbance numbers for different concentrations of added LSs [g LSs / 100 g binder] (left column) in ANL cement with addition of FA, scanned in Thermo Scientific Genesys 10S UV-VIS at 281 nm

	<b>ANL 30% FA IA</b>	<b>ANL 30% FA DA</b>	<b>ANL 60% FA IA</b>	<b>ANL 60% FA DA</b>
<b>0.05</b>		0.034		0.029
<b>0.1</b>	0.034	0.049	0.034	0.034
<b>0.2</b>	0.067	0.107	0.056	0.068
<b>0.4</b>	0.173	0.327	0.143	0.236
<b>0.8</b>	0.446	1.013	0.392	0.923
<b>1.2</b>	0.742	1.466	0.670	1.258
<b>1.5</b>	0.969		0.853	1.045

Table A.5 – Absorbance numbers for different concentrations of added LSs [g LSs / 100 g binder] (left column) in CX cement with addition of GGBFS, scanned in Thermo Scientific Genesys 10S UV-VIS at 281 nm

	<b>CX 30% GGBFS IA</b>	<b>CX 30% GGBFS DA</b>	<b>CX 60% GGBFS IA</b>	<b>CX 60% GGBFS DA</b>
<b>0.05</b>		0.052		0.052
<b>0.1</b>	0.075	0.089	0.077	0.078
<b>0.2</b>	0.133	0.156	0.141	0.154
<b>0.4</b>	0.257	0.385	0.274	0.369
<b>0.8</b>	0.616	0.944	0.672	0.903
<b>1.2</b>	0.948	1.811	1.091	1.885
<b>1.5</b>	0.925	2.322	1.219	

Table A.6 – Absorbance numbers for different concentrations of added LSs [g LSs / 100 g binder] (left column) in CX cement with addition of FA, scanned in Thermo Scientific Genesys 10S UV-VIS at 281 nm

	<b>CX 30% FA IA</b>	<b>CX 30% FA DA</b>	<b>CX 60% FA IA</b>	<b>CX 60% FA DA</b>
<b>0.05</b>		0.046		0.04
<b>0.1</b>	0.061	0.069	0.040	0.051
<b>0.2</b>	0.102	0.140	0.077	0.105
<b>0.4</b>	0.212	0.342	0.168	0.266
<b>0.8</b>	0.532	0.846	0.480	0.739
<b>1.2</b>	0.725	1.691	0.668	1.533
<b>1.5</b>	0.831	1.974	1.007	1.405

Table A.7 – Absorbance numbers for different concentrations of added LSs [g LSs / 100 g binder] (left column) in pure FA and GGBFS in distilled water with pH 7 and in APWS with pH 13, scanned in Thermo Scientific Genesys 10S UV-VIS at 281 nm

	<b>FA with pure water</b>	<b>GGBFS with pure water</b>	<b>FA with APWS</b>	<b>GGBFS with APWS</b>
<b>0.1</b>	0.037	0.110	0.107	0.290
<b>0.2</b>	0.062	0.229	0.285	0.791
<b>0.4</b>	0.186	0.485	1.384	1.766
<b>0.8</b>	0.690	1.304	2.939	3.170
<b>1.2</b>		1.938		3.928
<b>1.5</b>		2.514		3.966

Table A.8 – Absorbance numbers for LSs added as 0.4 g LSs / 100 g binder in neat ANL and CX for different hydration times in minutes, scanned in Thermo Scientific Genesys 10S UV-VIS at 281 nm

	<b>ANL</b>	<b>CX</b>
<b>10 min.</b>	0.212	0.266
<b>30 min.</b>	0.219	0.285
<b>60 min.</b>	0.159	0.207
<b>120 min.</b>	0.162	0.162
<b>180 min.</b>	0.140	0.140



Table A.9 – Consumed amount LSs in neat cements for different concentrations of added LSs (left column)

[g consumed LSs/100g cement]

	<b>ANL IA</b>	<b>ANL DA</b>	<b>CX IA</b>	<b>CX DA</b>
<b>0.05</b>		0.060		0.055
<b>0.1</b>	0.10	0.10	0.091	0.090
<b>0.2</b>	0.19	0.17	0.16	0.16
<b>0.4</b>	0.33	0.27	0.30	0.24
<b>0.8</b>	0.59	0.31	0.53	0.32
<b>1.2</b>	0.86	0.42	0.75	0.45
<b>1.5</b>	1.09	0.37	1.01	0.30

Table A.10 – Consumed amount LSs in ANL cement with addition of GGBFS for different concentrations of added LSs (left column)

[g consumed LSs/100g binder]

	<b>ANL 30% GGBFS IA</b>	<b>ANL 30% GGBFS DA</b>	<b>ANL 60% GGBFS IA</b>	<b>ANL 60% GGBFS DA</b>
<b>0.05</b>		0.058		0.059
<b>0.1</b>	0.11	0.10	0.12	0.10
<b>0.2</b>	0.19	0.17	0.20	0.18
<b>0.4</b>	0.33	0.23	0.36	0.30
<b>0.8</b>	0.59	0.41	0.63	0.36
<b>1.2</b>	0.83		0.88	
<b>1.5</b>	1.03		1.08	

Table A.11 – Consumed amount LSs in ANL cement with addition of FA for different concentrations of added LSs (left column)

[g consumed LSs/100g binder]

	<b>ANL 30% FA IA</b>	<b>ANL 30% FA DA</b>	<b>ANL 60% FA IA</b>	<b>ANL 60% FA DA</b>
<b>0.05</b>		0.064		0.068
<b>0.1</b>	0.11	0.11	0.12	0.12
<b>0.2</b>	0.20	0.18	0.21	0.20
<b>0.4</b>	0.35	0.27	0.37	0.31
<b>0.8</b>	0.61	0.34	0.65	0.34
<b>1.2</b>	0.87	0.51	0.92	0.57
<b>1.5</b>	1.06		1.13	0.98

Table A.12 – Consumed amount LSs in CX cement with addition of GGBFS for different concentrations of added LSs (left column)

[g consumed LSs/100g binder]

	<b>CX 30% GGBFS IA</b>	<b>CX 30% GGBFS DA</b>	<b>CX 60% GGBFS IA</b>	<b>CX 60% GGBFS DA</b>
<b>0.05</b>		0.055		0.055
<b>0.1</b>	0.094	0.088	0.093	0.093
<b>0.2</b>	0.17	0.16	0.16	0.16
<b>0.4</b>	0.31	0.25	0.30	0.25
<b>0.8</b>	0.54	0.39	0.51	0.40
<b>1.2</b>	0.79	0.38	0.71	0.34
<b>1.5</b>	1.10	0.45	0.95	

Table A.13 – Consumed amount LSs in CX cement with addition of FA for different concentrations of added LSs (left column)  
[g consumed LSs/100g binder]

	<b>CX 30% FA IA</b>	<b>CX 30% FA DA</b>	<b>CX 60% FA IA</b>	<b>CX 60% FA DA</b>
<b>0.05</b>		0.058		0.062
<b>0.1</b>	0.10	0.097	0.11	0.11
<b>0.2</b>	0.18	0.16	0.19	0.18
<b>0.4</b>	0.33	0.26	0.34	0.29
<b>0.8</b>	0.57	0.41	0.58	0.44
<b>1.2</b>	0.87	0.40	0.88	0.42
<b>1.5</b>	1.12	0.56	1.00	0.78

Table A.14 – Consumed amount LSs in pure FA and GGBFS in distilled water with pH 7 and in APWS with pH 13 for different concentrations of added LSs (left column). The calibration curve with LSs in distilled water are used.

[g consumed LSs/100g binder]

	<b>FA with pure water</b>	<b>GGBFS with pure water</b>	<b>FA with APWS</b>	<b>GGBFS with APWS</b>
<b>0.1</b>	0.12	0.077	0.074	-0.010
<b>0.2</b>	0.20	0.12	0.067	-0.15
<b>0.4</b>	0.33	0.20	-0.39	-0.42
<b>0.8</b>	0.42	0.20	-0.92	-0.70
<b>1.2</b>		0.29		-0.67
<b>1.5</b>		0.31		-0.39

Table A.15 – Added and consumed amount LSs in neat cements per surface area of binders  
[g LSs/m<sup>2</sup> cement]

Added	ANL		Added	CX	
	Consumed IA	Consumed DA		Consumed IA	Consumed DA
0.00056		0.00067	0.00038		0.00041
0.00112	0.00115	0.00111	0.00075	0.00069	0.00068
0.00225	0.00210	0.00192	0.00151	0.00122	0.00122
0.00449	0.00370	0.00300	0.00302	0.00225	0.00183
0.00899	0.00664	0.00344	0.00603	0.00403	0.00240
0.01348	0.00969	0.00473	0.00905	0.00566	0.00342
0.01685	0.01224	0.00415	0.01131	0.00758	0.00228

Table A.16 – Added and consumed amount LSs in ANL cement with addition of GGBFS per  
surface area of binders  
[g LSs/m<sup>2</sup> binder]

Added	ANL 30% GGBFS		Added	ANL 60% GGBFS	
	Consumed IA	Consumed DA		Consumed IA	Consumed DA
0.00058		0.00130	0.00061		0.00072
0.00117	0.00130	0.00221	0.00122	0.00133	0.00124
0.00233	0.00221	0.00388	0.00243	0.00225	0.00221
0.00467	0.00388	0.00685	0.00486	0.00384	0.00361
0.00933	0.00685	0.00973	0.00972	0.00691	0.00441
0.01400	0.00973		0.01458	0.01025	
0.01750	0.01197		0.01823	0.01245	

Table A.17 – Added and consumed amount LSs in ANL cement with addition of FA per surface area of binders  
[g LSs/m<sup>2</sup> binder]

Added	ANL 30% FA		Added	ANL 60% FA	
	Consumed IA	Consumed DA		Consumed IA	Consumed DA
0.00046		0.00041	0.00038		0.00052
0.00092	0.00105	0.00069	0.00076	0.00088	0.00088
0.00185	0.00183	0.00115	0.00153	0.00156	0.00151
0.00369	0.00319	0.00185	0.00305	0.00273	0.00235
0.00738	0.00565	0.00292	0.00611	0.00477	0.00262
0.01107	0.00801	0.00280	0.00916	0.00670	0.00432
0.01384	0.00975	0.00394	0.01145	0.00825	0.00747

Table A.18 – Added and consumed amount LSs in CX cement with addition of GGBFS per surface area of binders  
[g LSs/m<sup>2</sup> binder]

Added	CX 30% GGBFS		Added	CX 60% GGBFS	
	Consumed IA	Consumed DA		Consumed IA	Consumed DA
0.00043		0.00047	0.00050		0.00055
0.00086	0.00081	0.00075	0.00100	0.00093	0.00092
0.00171	0.00143	0.00134	0.00199	0.00163	0.00156
0.00343	0.00265	0.00214	0.00399	0.00299	0.00254
0.00686	0.00465	0.00333	0.00798	0.00510	0.00401
0.01028	0.00675	0.00330	0.01196	0.00711	0.00336
0.01285	0.00941	0.00383	0.01496	0.00949	

Table A.19 – Added and consumed amount LSs in CX cement with addition of FA per surface area of binders

[g LSs/m<sup>2</sup> binder]

<b>CX 30% FA</b>			<b>CX 60% FA</b>		
Added	Consumed IA	Consumed DA	Added	Consumed IA	Consumed DA
		0.00043	0.00033		0.00041
0.00071	0.00072	0.00071	0.00066	0.00074	0.00070
0.00141	0.00128	0.00120	0.00132	0.00127	0.00117
0.00283	0.00231	0.00199	0.00264	0.00227	0.00193
0.00566	0.00402	0.00325	0.00528	0.00381	0.00290
0.00849	0.00617	0.00347	0.00792	0.00579	0.00274
0.01061	0.00793	0.00471	0.00990	0.00657	0.00517

Table A.20 – Added and consumed amount LSs in pure FA and GGBFS in distilled water with pH 7 and in APWS with pH 13. The calibration curve with LSs in distilled water are used.

[g LSs/m<sup>2</sup> binder]

<b>FA</b>			<b>GGBFS</b>		
Added	Consumed distilled water	Consumed APW	Added	Consumed distilled water	Consumed APW
0.00060	0.00069	0.00044	0.00129	0.00100	-0.00013
0.00119	0.00119	0.00040	0.00258	0.00154	-0.00197
0.00238	0.00194	-0.00233	0.00515	0.00252	-0.00547
0.00476	0.00253	-0.00549	0.01031	0.00257	-0.00908
			0.01546	0.00376	-0.00865
			0.01933	0.00404	-0.00503

Table A.21 – Consumed amount LSs in neat ANL and CX for different hydration times in minutes, scanned in Thermo Scientific Genesys 10S UV-VIS at 281 nm. The LSs was added as 0.4 g LSs / 100 g binder for all samples.

[g LSs/100 g cements]

	ANL	CX
<b>10 min.</b>	0.33	0.31
<b>30 min.</b>	0.33	0.30
<b>60 min.</b>	0.36	0.33
<b>120 min.</b>	0.36	0.35
<b>180 min.</b>	0.37	0.36





# Appendix B

## pH values

Table B.1 – Measured pH values for ANL cement with and without mineral admixtures and with immediate and delayed addition of LSs

	<b>ANL</b>	<b>ANL 30% GGBFS</b>	<b>ANL 60% GGBFS</b>	<b>ANL 30% FA</b>	<b>ANL 60% FA</b>
<b>0</b>	13.06	12.91	12.82	12.91	12.86
<b>0.4 IA</b>	13.02	12.92	12.75	12.89	12.78
<b>0.8 IA</b>	12.96	12.80	12.59	12.94	12.78
<b>0.4 DA</b>	12.92	12.92	12.75	12.86	12.80
<b>0.8 DA</b>	12.91	12.74	12.60	12.76	12.67

Table B.2 – Measured pH values for CX cement with and without mineral admixtures and with immediate and delayed addition of LSs

	<b>CX</b>	<b>CX 30% GGBFS</b>	<b>CX 60% GGBFS</b>	<b>CX 30% FA</b>	<b>CX 60% FA</b>
<b>0</b>	13.20	13.18	13.04	13.17	12.96
<b>0.4 IA</b>	13.16	13.10	12.97	13.06	12.96
<b>0.8 IA</b>	13.24	13.22	12.95	13.30	13.07
<b>0.4 DA</b>	13.15	13.06	12.89	13.07	12.92
<b>0.8 DA</b>	13.08	13.01	12.77	13.00	12.87

Table B.3 – Measured pH values for fly ash and GGBFS with and without addition of LSs in distilled water with pH 7 and APW with pH 13 and with immediate addition of LSs

	<b>100% FA</b>	<b>100% GGBFS</b>	<b>100% FA APW</b>	<b>100% GGBFS APW</b>
<b>0</b>	10.5	11.89	11.29	12.88
<b>0.4 IA</b>	10.6	11.36	10.67	12.73
<b>0.8 IA</b>	10.71	11.02	10.53	12.27

# Appendix C

## Repeatability: averages and standard deviations

Table C.1 – Averages and standard deviations for ANL cement with FA for different concentrations added LSs and addition time (left column). The three repeated absorbance numbers and averages are shown. The two right columns contain the standard deviations for the calculated amount consumed LSs per weight of binder and per surface area of binders. The coefficient of variation is calculated as the standard deviation of binders divided on the amount added LSs.

	Repeated abs. numbers			Average	Standard deviation		Coefficient of variation
	No. 1	No. 2	No. 3		Weight of binders	Surface area of binders	
<b>30% replacement of FA</b>							
<b>0.1 IA</b>	0.034	0.034	0.033	0.034	0.00028	2.603E-06	0.28
<b>0.4 IA</b>	0.168	0.176	0.175	0.173	0.00213	1.965E-05	0.53
<b>1.2 IA</b>	0.734	0.731	0.761	0.742	0.00808	7.452E-05	0.67
<b>0.1 DA</b>	0.049	0.050	0.048	0.049	0.00049	4.510E-06	0.49
<b>0.4 DA</b>	0.285	0.404	0.292	0.327	0.03265	0.000301	8.16
<b>1.2 DA</b>	1.033	1.705	1.66	1.466	0.18366	0.00169	15.30
<b>60% replacement of FA</b>							
<b>0.1 IA</b>	0.037	0.033	0.031	0.034	0.00162	1.237E-05	1.62
<b>0.4 IA</b>	0.148	0.146	0.135	0.143	0.00371	2.835E-05	0.93
<b>1.2 IA</b>	0.672	0.666	0.673	0.670	0.00201	1.533E-05	0.17
<b>0.1 DA</b>	0.038	0.029	0.034	0.034	0.00239	1.826E-05	2.39
<b>0.4 DA</b>	0.234	0.207	0.266	0.236	0.01567	0.000120	3.92
<b>1.2 DA</b>	1.378	1.184	1.211	1.258	0.05576	0.000425	4.65

Table C.2 – Averages and standard deviations for ANL cement with GGBFS for different concentrations added LSs and addition time (left column). The three repeated absorbance numbers and averages are shown. The two right columns contain the standard deviations for the calculated amount consumed LSs per weight of binder and per surface area of binders. 1.2 g LSs / 100 g binder was not measurable for DA. The coefficient of variation is calculated as the standard deviation of binders divided on the amount added LSs.

	Repeated abs. numbers			Average	Standard deviation		Coefficient of variation
	No. 1	No. 2	No. 3		Weight of binders	Surface area of binders	
<b>30% replacement of GGBFS</b>							
<b>0.1 IA</b>	0.040	0.037	0.038	0.038	0.00071	8.237E-06	0.71
<b>0.4 IA</b>	0.214	0.210	0.203	0.209	0.00257	3.002E-05	0.64
<b>1.2 IA</b>	0.896	0.803	0.865	0.855	0.02188	0.000255	1.82
<b>0.1 DA</b>	0.063	0.062	0.063	0.063	0.00027	3.113E-06	0.27
<b>0.4 DA</b>	0.357	0.538	0.368	0.421	0.04690	0.000547	11.72
<b>60% replacement of GGBFS</b>							
<b>0.1 IA</b>	0.044	0.043	0.042	0.043	0.00047	5.727E-06	0.47
<b>0.4 IA</b>	0.245	0.242	0.238	0.242	0.00166	2.011E-05	0.41
<b>1.2 IA</b>	0.818	0.829	0.809	0.819	0.00472	5.736E-05	0.39
<b>0.1 DA</b>	0.063	0.051	0.062	0.059	0.00314	3.813E-05	3.14
<b>0.4 DA</b>	0.282	0.282	0.28	0.281	0.00054	6.613E-06	0.13

Table C.3 – Averages and standard deviations for CX cement with FA for different concentrations added LSs and addition time (left column). The three repeated absorbance numbers and averages are shown. The two right columns contain the standard deviations for the calculated amount consumed LSs per weight of binder and per surface area of binders. The coefficient of variation is calculated as the standard deviation of binders divided on the amount added LSs.

	<b>Repeated abs. numbers</b>				<b>Standard deviation</b>		
	<b>No. 1</b>	<b>No. 2</b>	<b>No. 3</b>	<b>Average</b>	<b>Weight of binders</b>	<b>Surface area of binders</b>	<b>Coefficient of variation</b>
<b>30% replacement of FA</b>							
<b>0.1 IA</b>	0.065	0.059	0.058	0.061	0.00187	1.322E-05	1.87
<b>0.4 IA</b>	0.199	0.218	0.22	0.212	0.00572	4.046E-05	1.43
<b>1.2 IA</b>	0.587	0.861	0.728	0.725	0.06764	0.000478	5.64
<b>0.1 DA</b>	0.068	0.072	0.066	0.069	0.00151	1.067E-05	1.51
<b>0.4 DA</b>	0.343	0.342	0.342	0.342	0.00029	2.015E-06	0.07
<b>1.2 DA</b>	1.561	1.732	1.779	1.691	0.05664	0.000401	4.72
<b>60% replacement of FA</b>							
<b>0.1 IA</b>	0.039	0.042	0.04	0.040	0.00082	5.382E-06	0.82
<b>0.4 IA</b>	0.166	0.169	0.17	0.168	0.00111	7.334E-06	0.26
<b>1.2 IA</b>	0.681	0.632	0.69	0.668	0.01666	0.000110	1.39
<b>0.1 DA</b>	0.054	0.051	0.049	0.051	0.00134	8.867E-06	1.34
<b>0.4 DA</b>	0.250	0.271	0.276	0.266	0.00736	4.861E-05	1.84
<b>1.2 DA</b>	1.633	1.337	1.630	1.533	0.09076	0.000599	7.56

Table C.4 – Averages and standard deviations for CX cement with GGBFS for different concentrations added LSs and addition time (left column). The three repeated absorbance numbers and averages are shown. The two right columns contain the standard deviations for the calculated amount consumed LSs per weight of binder and per surface area of binders. The coefficient of variation is calculated as the standard deviation of binders divided on the amount added LSs.

	Repeated abs. numbers			Average	Standard deviation		Coefficient of variation
	No. 1	No. 2	No. 3		Weight of binders	Surface area of binders	
<b>30% replacement of GGBFS</b>							
<b>0.1 IA</b>	0.069	0.077	0.079	0.075	0.00247	2.115E-05	2.47
<b>0.4 IA</b>	0.260	0.249	0.263	0.257	0.00344	2.946E-05	0.86
<b>1.2 IA</b>	0.964	0.939	0.940	0.948	0.00660	5.657E-05	0.55
<b>0.1 DA</b>	0.093	0.087	0.086	0.089	0.00177	1.513E-05	1.77
<b>0.4 DA</b>	0.384	0.373	0.398	0.385	0.00584	5.008E-05	1.46
<b>1.2 DA</b>	1.926	1.940	1.568	1.811	0.09834	0.0008426	8.19
<b>60% replacement of GGBFS</b>							
<b>0.1 IA</b>	0.072	0.076	0.083	0.077	0.00264	2.631E-05	2.64
<b>0.4 IA</b>	0.278	0.275	0.269	0.274	0.00217	2.165E-05	0.54
<b>1.2 IA</b>	1.092	1.094	1.087	1.091	0.00171	1.703E-05	0.14
<b>0.1 DA</b>	0.077	0.080	0.078	0.078	0.00072	7.217E-06	0.72
<b>0.4 DA</b>	0.371	0.376	0.361	0.369	0.00362	3.608E-05	0.90
<b>1.2 DA</b>	1.887	1.867	1.901	1.885	0.00810	8.073E-05	0.67

Table C.5 – Averages and standard deviations for measured pH values for ANL cement

	Repeated values for ANL			Average	Standard deviation
	No. 1	No. 2	No. 3		
<b>0</b>	13.07	13.06	13.04	13.06	0.0153
<b>0.8 IA</b>	12.95	12.95	12.98	12.96	0.0173
<b>0.8 DA</b>	12.91	12.94	12.87	12.91	0.0351

Table C.6 – Averages and standard deviations for measured pH values for CX cement

	Repeated values for CX			Average	Standard deviation
	No. 1	No. 2	No. 3		
<b>0</b>	13.17	13.20	13.24	13.20	0.0351
<b>0.8 IA</b>	13.21	13.22	13.30	13.24	0.0493
<b>0.8 DA</b>	13.06	13.06	13.11	13.08	0.0289