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# Adsorption of plasticizers on Portland cement surface

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<p>Työn tarkoituksena oli tutustua sementin valmistukseen ja valmistuksessa käytettäviin lisä-aineisiin. Työssä tutkittiin erityisesti notkistimien käyttöä sekä niiden adsorption tutkimismenetelmiä ja tarkoituksena oli löytää menetelmä, jolla adsorptiota portlandsementti (CEM I) -partikkelin pinnassa voi mitata. Työssä oli tutkittavana kaksi kaupallista notkistinta sekä kaksi uutta ligniinipohjaista notkistinta. Työ tehtiin VTT Oy:lle.</p> <p>Työssä esiteltiin ensin kirjallisuuden pohjalta, mitä on adsorptio, sen isotermejä, betonin valmistusta ja siinä käytettäviä lisäaineita. Sen jälkeen tutkittiin raporttien pohjalta erilaisia menetelmiä analysoida notkistimien adsorptiokykyä ja tehtiin menetelmä, joka yhdisteli eri vaiheita näistä raporteista.</p> <p>Työssä tehtiin pieniä sementtipastanäytteitä sekoittamalla vettä, sementtiä ja notkistinta keskenään. Tämä sekoitettu pasta lingottiin sentrifugilla. Lingotusta näytteestä erotettiin pipetoimalla nestettä, joka suodatettiin. Suodoksesta mitattiin adsorboitumattoman notkistimen määrä UV-spektrofotometrillä. Kaupallisista notkistimista 1-prosentin annostelulla oli yli 40 % adsorboitunut sementin pintaan, ja käyrien mukaan adsorptio olisi jatkunut. Ligniinipohjaisista 1 -prosentin annostelu tuotti noin 30-prosenttisen adsorption ja adsorptiomaksimi löydettiin.</p> <p>Käytetty menetelmä oli helppo ja tarkan oloinen. Sitä tutkiessa hajonta oli pientä kaikkien vaiheiden kohdalla, mikä loi tarkkoja tuloksia. Tulokset näyttivät käyttäytyvän oletetun Langmuirin isotermin mukaisesti. Tuloksissa huomattiin myös notkistimen isomman partikkelikoon adsorboituvan helpommin sementin pinnalle, kuin pienemmät partikkelikoot.</p>	
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<p>The purpose of the thesis was to study the manufacture of cement and the additives used in this process. The research was focused on the use of plasticizers, and on the methods of researching their adsorption. The aim was to find a way to measure adsorption on the surface of the Portland cement (CEM I) particle. Two commercial plasticizers were analyzed, as well as two new lignin-based plasticizers. The work was carried out for VTT Oy.</p> <p>Literature was studied to define adsorption and to describe its isotherms, concrete production and the additives used in it. Then, On the basis of other reports, various methods to analyze the ability of plasticizer adsorption were investigated to form a method that combined the various steps from these reports.</p> <p>Small cement paste samples were made by mixing water, cement, and plasticizer with each other. These paste samples were centrifuged. The centrifuged samples were separated by pipetting the liquid which was then filtered. The amount of unadsorbed plasticizer was measured by the UV spectrophotometer. Over 40% of commercial plasticizers with a dose of 1% adsorbed, and according to graphs, the adsorption would have continued. About 30% of the lignin-based plasticizers with a dose of 1% adsorbed, and the adsorption maximum were found.</p> <p>The method used was easy and accurate. When analyzing the method, the dispersion was small for all phases, producing accurate results. The results behaved like the Langmuir isotherm. The results also revealed that the larger particle size was adsorbed more easily on the surface of the cement particle than the smaller ones.</p>	
Keywords	cement, adsorption, plasticizer

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## Abbreviations

LS	Lignosulfonates
TOC	Total organic carbon
UV	Ultraviolet
PNS	Polynaphtalenesulfonate
CaCl <sub>2</sub>	Calcium chloride
rpm	Rounds per minute
SEC	Size-exclusion chromatography

## 1 Introduction

In concrete production, water is mandatory. The amount of water makes the concrete workable, but also have effects on the mechanical and durability properties of concrete. Water and cement ratio is the most important factor that affects the strength and life expectancy of concrete. Plasticizer's function is to reduce the amount of water needed in the process and make the fresh concrete more workable. Plasticizers are additives that adsorb on cement particles by electrostatic forces. Cement has  $\text{Ca}^{2+}$  -sites that the negatively charged plasticizer can use to adsorb on the particles. (Cabrera and Rivera-Villarreal, 1999)

There are two ways the plasticizer can repulse or hinder water getting trapped. These two are electrostatic repulsion and steric repulsion. In electrostatic repulsion, cement particles become negatively charged, and they start to repel each other because of the same charge. In steric repulsion, the particles have adsorbed polycarboxylate chains that do make a small barrier that keeps the particles away. (Physical Stability of Disperse Systems, 2009). A schematic presentation of the two alternative stabilization mechanisms is shown in Figure 1. (Physical Stability of Disperse Systems, 2009)

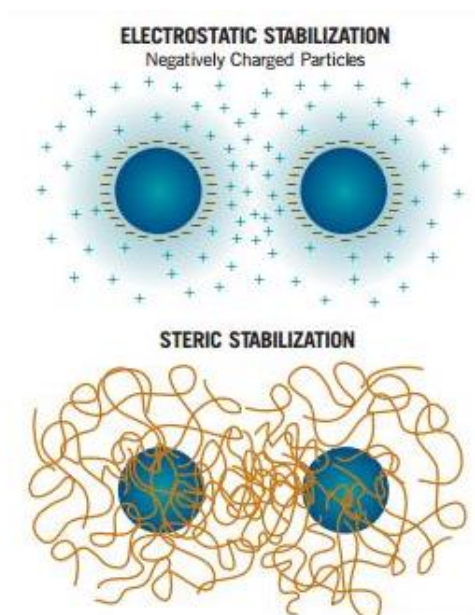


Figure 1. Electrostatic and steric stabilizations.

The theses includes a literature review and an experimental part. The review concentrates on concrete production and different types of concrete additives. The review will

help to understand why and how different types of additives function and to help to develop a method for quantifying plasticizer adsorption on cement. In the experimental part four different plasticizers, two being in commercial use and two under development are studied

## 2 Adsorption

Adsorption is an ability of a substance to stick on to a surface of another substance. The substance makes a thin layer on top of the surface. Every adsorbate has its capacity and ability to adsorb on to solid surfaces. Adsorption can happen between different interfaces: gas-liquid, liquid-liquid, gas-solid and liquid-solid. The first part of the interface name tells the phase of the adsorbate that will become adsorbed, and the second part of the interface tells the adsorbent that will get liquid adsorbing on it.

### 2.1 Liquid-solid interphase adsorption

In liquid-solid interphase, adsorbate is the liquid that gets adsorbed on the surface of adsorbent that is solid. An electromagnetic force from free ions in liquid pulling closer to the solid that is oppositely charged. Liquid-solid adsorption is commonly used as a cleaning mechanism and in dispersing. Plasticizer adsorption on cement surface is liquid-solid adsorption. The plasticizer is the adsorbate and The cement is the adsorbent. (Barnes and Gentle, 2005)

### 2.2 Isotherms

Isotherms are a way to estimate the adsorption behavior. Estimation of liquid-solid adsorption can be calculated the same way as gas-solid when the concentration is small enough, and the solid is a monolayer. The two isotherms usually used with gas-solid adsorption are Langmuir- or Freundlich isotherms. Freundlich isotherm is entirely empirical isotherm so it can have problems. With new materials, Freundlich isotherm is hard to compare with anything already done. The base equation can change with the material. Thus, new materials do not have a comparing point. Langmuir Offers a similar explanation, but it is more based on theories than the Freundlich isotherm. Therefore, it is usable in experimental work. (Freundlich Adsorption Isotherm, 2017)



In Langmuir isotherm's theory, solid has a surface area that can adsorb gas on to it. The surface will get covered more by increasing pressure in the system, until the gas fully covers the surface. At the start, small increases will cover more of the solid surface, but towards the end, it will slow down. This effect can be seen in Figure 2. Although Langmuir isotherm is used to describe the gas-solid interface, it can be tailored to a liquid-solid interface. The system must be a monolayer, meaning that adsorption is happening on one layer, and the amount of pressure can be changed to the amount of liquid in the system. (Barnes and Gentle, 2005)

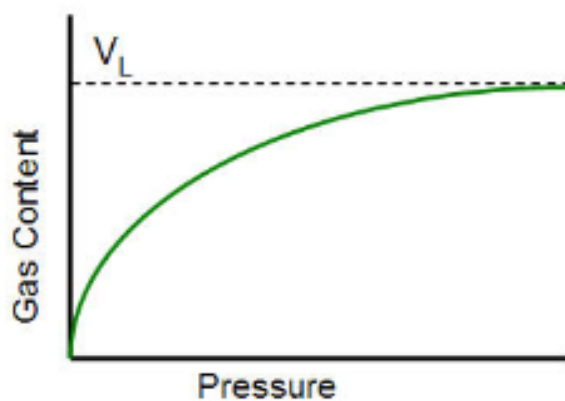


Figure 2. Langmuir isotherm in graph form. (*Langmuir isotherm*, 2014)

### 3 Concrete manufacturing

Concrete contains cement, sand, gravel, and water. When cement comes in to contact with water, the hydration process starts. This process happens in two stages. In the first stage, the concrete paste starts to hydrate. The concrete is workable for a couple of hours. During this time, it is cast and left to set. After that, concrete starts to take a form where it is not workable anymore but still lacks the strength. Usually, this takes one to six hours. In the second stage, it starts to get the strength required for the concrete in that specific process. The full process takes 91 days.

Sometimes concrete can have additives mixed in it. These additives help in the manufacturing process in different stages. They can speed up the strengthening process to get the minimum strength needed faster or to slow the setting time to get more time to work with it. (Lampinen and Honkavuori, 1985)

### 3.1 Cement

Cement is a necessary part of the concrete. Cement binds all the other materials together like sand and gravel, which are aggregates in concrete. Portland cement is made from 95 % to 100% Portland clinker. Portland clinker is raw material mixture primarily made of calcium oxides, silicate oxides, aluminum oxides and ferric oxides. Other types of cement have less clinker in them but have other materials compensating for it. These materials might be blast-furnace slag, pozzolana, fly ash, silica or limestone. Cement can also be categorized as hydraulic or non-hydraulic, depending on the cement's ability set in the presence of water. Temperature is also an essential factor in concrete making. In lower temperatures, hydration reactions of cement become slower. Cement can be categorized into five different types (Table 1). (Lampinen and Honkavuori, 1985)

Table 1. Cement types and their descriptions (SFS-EN 197-1, (2012:01))

<b>Cement Type</b>	<b>Description</b>
Cem I	Portland cement
Cem II	Portland mixture cement
Cem III	Blast-furnace slag cement
Cem IV	Pozzolane cement
Cem V	Mixture cement

### 3.2 Additives

In concrete manufacturing, different admixtures are used to help the manufacturing process. Each of them has their function. An additive is chosen based on what properties the concrete needs for successful construction.

#### 3.2.1 Accelerators

The accelerators speed mainly the strengthening process, but some of them have properties that can be used to control bonding time. Control of the bonding time is beneficial if casting needs to be done quickly. In winter, the faster reaction in concrete creates more heat in the composition, which speeds up strengthening the process. Therefore, accelerators are even more useful when the temperature is low. Problem with accelerator use

is that after heat treatment they may increase the loss of strength. The most effective accelerator is  $\text{CaCl}_2$ . Its addition is between 2 to 4 percent of the weight of cement. Because of corrosion-increasing effects, the use of  $\text{CaCl}_2$  accelerator has been reduced. More used accelerators now days are other salts or accelerators that are based on crystallizing process. The working mechanism of accelerators is not fully understood. (Michaux, Nelson and Vidick, 1989)

### 3.2.2 Plasticizer

Plasticizers are also called as dispersants. Plasticizers neutralize positive charges on cement particles. They break up aggregates into individual particles. Plasticizers help to make cement more homogenous and lower its permeability. The most common ones are polycarboxylates. (Michaux, Nelson and Vidick, 1989)

### 3.2.3 Retarders

Retarders delay the setting time of cement slurry by reducing the heat production, which is a problem in massive constructions. Retarders are used when the concrete needs to be transported long ways. They are also useful in places where transition needs to be seamless, due to the increased work time with the cement. Retarders can also be used if the setting of all the concrete elements is wanted to start at the same time. Retarders cannot counteract the loss of cement pastes own plasticizing effect. Retarders are dosed in small amounts; thus, overdosing is possible and might slow the process for weeks (Lampinen and Honkavuori, 1985). The way retarders work is still not completely understood. The most common retarders are by-products of wood pulping. They comprise of lignosulfonate acids and contain some saccharides. (Michaux, Nelson and Vidick, 1989)

### 3.2.4 Air-entrainment agent

Air-entrainment agent is additive that improves frost resistance. It creates small air bubbles in concrete. The pores increase concrete workability, has plasticizing, and cohesive effects and reduce components separation. Addition of air-entrainment agent is done when concrete is relatively plasticized and does not have many fine aggregates. Air-entrainment is hard to adjust if the amount of cement is high. It is also possible to improve the frost resistance of concrete more with micro air-entrainments. Because of their

smaller size, they are needed less than their standard size counterparts, and because micro air-entrainments are small, they do not have a significant effect on the amount of cement paste. (Lampinen and Honkavuori, 1985)

## **4 Concrete Plasticizers**

Plasticizers are also a group of additives used in concrete manufacturing. Typical plasticizers include sulfonated alkali salts of naphthalene or melamine formaldehyde polymers, or sodium or calcium salts of lignosulfonate acids as well as specific hydroxycarboxylic acids and their alkali salts. (Kamoun, Jelidi and Chaabouni, 2003)

### 4.1 Types

Plasticizers are separated into two categories. Plasticizers and superplasticizers Plasticizer reduce the required water by 4-12% and the superplasticizer at least 12%. The water reduction is determined using a given standard SFS-EN 934-2 + A1 (2013:01)

#### 4.1.1 Plasticizer

Different plasticizers used are lignosulfonates, melamine sulfonates, naphtha sulfonate and polycarboxylates. Lignin is one of the main components of all woody plants. Lignin content in wood ranges 15-40% depending on the species. Lignosulfonates are products from sulfite pulping. They are used in concrete mixtures reducing the quantity of water needed by 4-10%. Lignosulfonates also have other uses, e.g., in animal food pellets and oil well-related applications. (Ratinac, Standard and Bryant, 2004).

#### 4.1.2 Superplasticizers

The industry has since made superplasticizers that decrease the amount of water needed to up to 30%. The lower water to cement ratio makes the concrete harder, and the superplasticizers make the handling of the fresh concrete easier by increasing concrete's workability.

## 4.2 Postulated working mechanism

Plasticizer aids the workability of fresh concrete with steric- or electrostatic repulsion. These repulsions keep the cement particles away from each other, leaving space between them for hydration process. A good plasticizer will not slow the process of hydration and lowers the amount of water needed to get the same workability. The water might get trapped in parts that are already hydrated, and the plasticizer tries to prevent this. This freeing of water will let the still hydrating parts access more water and get hydrated. Water amount should not be lowered under 30 %-w of cement. This water amount would lead to a point where all the cement will not get hydrated.

## 5 Plasticizer adsorption on cement

### 5.1 Methods used for studying adsorption

Publications introduced three different ways to follow the unadsorbed amount of the plasticizer in the water phase of cement paste. TOC analysis was used in the first publication to measure the total amount of carbon in the solution. This method is usable for all plasticizers. The method is not the easiest and is more time consuming than the others. (Zhang *et al.*, 2015) The second method is based on using UV-spectrophotometric detection of the plasticizer. In UV-spectrophotometric detection, the light was directed through the solution to measure how much light absorbs into the solution. This way, the unadsorbed material can be measured. (Kim *et al.*, 2000) The method is quick and straightforward, but it cannot measure plasticizers that do not absorb UV-light. The third method applied light scattering detection. (Akhlaghi *et al.*, 2017)

Separation of the liquid and cement was also done with three alternative methods. Polycarboxylate (PC) and  $\beta$ -naphthalene sulfonate (BNS) plasticizers used a method using a suction pump that would suck the suspension through a filter separating the cement from everything else. (Yoshioka *et al.*, 2002) The PNS used pressure filtering as a separation method. The water was pushed through a filter to separate the cement. (Hsu *et al.*, 1999) Another PC plasticizer and modified polycarboxylate ether (AMPS-PCE) applied centrifugation to separate the cement and the liquid. The centripetal force would

push the cement particles to the side and bottom of the container and water on top. Making two separate phases that they then put through a filter. (Akhlaghi *et al.*, 2017)

Table 2. Summary of the methods used for studying adsorption.

Plasticizer	Cement type	W/C ratio	Separation	Analyze method	Isotherm	Wavelength	Publication
BNS, PC	Portland, C3A, C4AF, C3S & C2S	2000 %	suction pump	TOC	mostly Langmuir		Yoshioka <i>et al.</i> , 2002
PC	Portland, Chinese standard	0,4	centrifuge	TOC			Zhang <i>et al.</i> , 2015
PNS	Portland	35	pressure filtering	UV		230+276+294	Kim <i>et al.</i> , 2000
SNF	Portland	50000 %		UV	Langmuir	280	Hsu <i>et al.</i> , 1999
AMPS-PCE	OPC-CEM 1 42.5 R	0,4	centrifuge	scatter light			Akhlaghi <i>et al.</i> , 2017

## 6 Experimental work

Adsorption is hard to measure from fully reacted concrete. It is easier to calculate the plasticizer that did not adsorb on to the cement particles. Unadsorbed parts can be measured easily merely with overdosing the amount of water. After cement and water are mixed just need to be separated by a certain amount of time. When the water is then examined, there will be traces of the plasticizer left. With small dosages most of the plasticizer will likely be adsorbed, but when increasing the concentration, the amount found in the water phase will increase to a point where the plasticizer mostly covers cement surfaces. Plasticizer will find a point that it cannot adsorb anymore on the cement particle and the extra will remain in the water phase. Publications that used UV-light to measure the absorption of a sample used the same principle to measure unadsorbed plasticizer (Kim *et al.*, 2000)

## 6.1 Preparation of cement paste

Portland cement CEM I 52.5 N (Finnsementti) was used to make the cement paste. For each experiment, 300 g of the cement was weighed. Water-cement ratio of 1:1 was used in all the experiments. The plasticizer products (solutions) studied as well as their active matter content are shown in Table 3. Plasticizers were dosed based on cement. Several dosages, in a range of 0.1–1 wt-% of the active matter on cement were used (Table 4). Sulfonated naphthalene formaldehyde (SNF) and lignosulphonate are commercial plasticizers that were analyzed. LigniOx plasticizers were alkali-O<sub>2</sub> oxidized lignins currently under development at VTT. (Kalliola *et al.*, 2015)

Table 3. Different plasticizers used.

Shortcode	Plasticizer	Trade name	Provider	Dry/active matter, %
A	Sulfonated naphthalene formaldehyde	Pantarhit FM LK	Ha-Be Betonchemie GmbH & CO. KG	40
B	Lignosulfonate	DP-3240	Borregaard AS	40
C	LigniOx	-	-	9.72
D	LigniOx	-	-	9.95

Table 4. Used plasticizer dosing, wt-% of the active matter, on cement.

Plasticizer A	Plasticizer B	Plasticizer C	Plasticizer D
0.10 %	0.10 %	0.05 %	0.10 %
0.30 %	0.25 %	0.15 %	0.15 %
0.50 %	0.50 %	0.30 %	0.30 %
1 %	1 %	0.50 %	0.50 %
		1 %	1 %

Mixing of the paste was made with the planetary mixer (Hobart: N-50G) with the lowest gear for 3 minutes. Timing was started when water first got in contact with cement. The mixer is shown in Figure 3. Cement mixing was tried with higher speeds, but the increase in the number of air bubbles made the paste hard to extract in the later stage. Water was poured in the first 30 seconds, leaving some plasticizer to rinse into the cement. After 30 seconds the plasticizer was poured into the paste, and the container was rinsed with water three times into the cement paste to get all the plasticizer in it. At one-minute mark,

the mixer was stopped for 30 seconds to scrape the sides of the bowl. Then the mixing process was continued and ended at the 3-minute mark.



Figure 3. Hobart: N-50G, planetary mixer, and a mixing bowl.

## 6.2 Separation of water phase

After the mixing, the paste was put into three tubes with a spoon. The tubes with the sample were weighted to be close to same weight than one counterweight. The samples weight was  $42.75 \text{ g} \pm 0.05 \text{ g}$ . This fluctuation was that the centrifuge (Hettich: universal 16) would still work. The maximum difference in mass could be 0.1g. The centrifuge can be seen in Figure 4. Between every filled tube, the paste was stirred hard with a spoon to keep the consistency. All the 3 sample tubes were put in the centrifuge in a metal holder. Metal holders were placed in a way that two tubes would be across from each



other. This placement can be seen in Figure 5. The centrifuge was then given parameters: 10 minutes of centrifuging with a speed of 4000 rpm. Centrifuging was started 10-minutes after the water first got in to contact with cement.

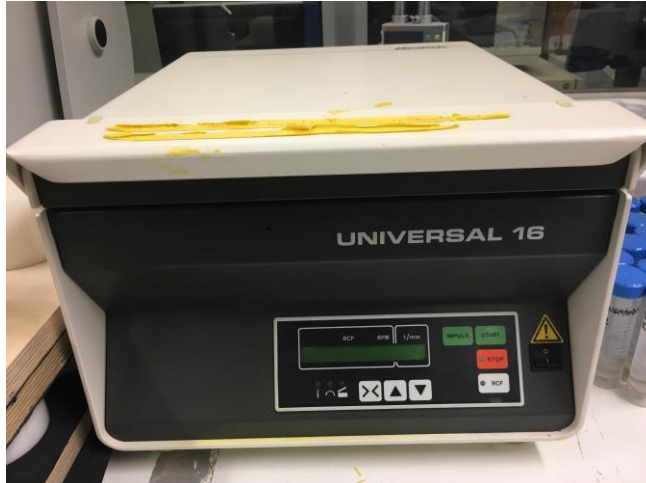


Figure 4. Hettich centrifuge.



Figure 5. Metal holders in a centrifuge.

After centrifuging, the separated liquid was pipetted into smaller tubes. In a way that the pipet would never touch the cement paste. At first, all samples from centrifuge were put in different test tubes and after couple tests all in the same tube. These tubes would then go through UV-spectrophotometer testing. The test tubes with the samples for next stage can be seen in Figure 6.

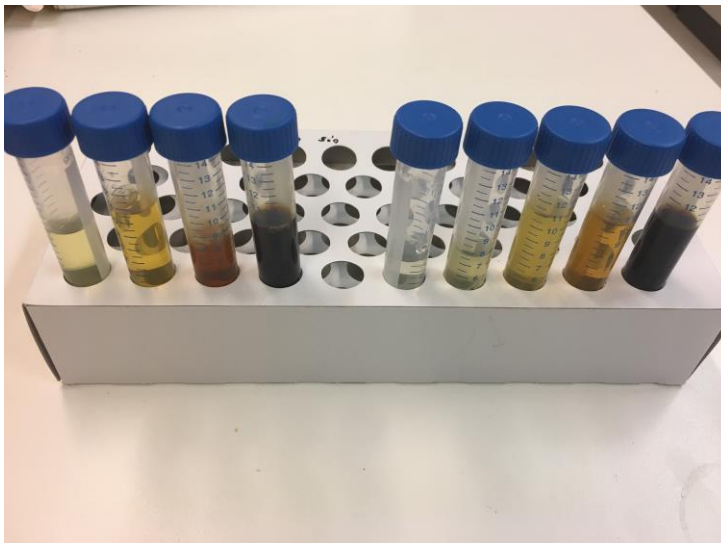


Figure 6. Plasticizer C and D samples with increasing dosing.

### 6.3 Measuring the absorption

After getting the samples from the centrifuge, the samples were filtered through 0.2 membrane filter to get the free cement particles away from the liquid that would block some of the light. With a liquid that was filtered, a good dilution ratio had to be found to get reliable and measurable results. When the plasticizer concentration increased in the water phase, the dilution ratio was also increased. To get reliable results, the absorbance value needs to be under 0.8. This maximum absorbance is apparatus based. Measurements are not in the linear part after absorbance value of 0.8 and might differ from the real number.

The samples were analyzed with a UV-spectrophotometer (Shimadzu UV-1800) (Figure 7) using quartz cuvettes of 1 cm diameter with water as a blank sample. From the samples, a whole spectrum from 200nm to 400nm was gathered. The spectrum was gathered to find the absorption peak of the plasticizers. The data for the whole spectrum was gathered, and with plasticizers A and B the logical point to be analyzed was decided on the basis of the data. For plasticizers C and D the absorption was already determined by (Kalliola *et al.*, 2015) Plasticizer A were recorded having the two peaks like in the publications, the higher wavelength of about 280 nm was used. Plasticizer B had only one peak, and it was recorded at 287. The applied wavelengths of the different plasticizers for computing the un-absorbed plasticizer amounts are shown in Table 5. Absorbance graphs can be seen in Appendix 1.



Figure 7. Shimadzu UV-1800

Table 5. Wavelength used for the plasticizers

Different plasticizer	Wavelength
Plasticizer A	280
Plasticizer B	287
Plasticizer C	280
Plasticizer D	280

Also, a sample with a given concentration of plasticizer A and B was measured in the same way. On the basis of these measurements, molar absorption coefficients ( $\epsilon$ ) for these plasticizers were computed. For plasticizers C and D an absorption coefficient of 25 was used.

## 6.4 Adsorption analysis

### 6.4.1 UV-measurements and Lambert-Beer's law

Lambert-Beer's law (Equation 1) is the basis of the spectrophotometric determinations. It explains that in an ideal solution, the dissolved solution's concentration and absorbance relation is linear if the distance that the light travels is constant. Every substance

has its coefficient, and through that, the concentration of each substance can be determined. (Heiskanen, 2016)

$$A = \log\left(\frac{P_{\lambda}^0}{P_0}\right) = \epsilon cl, \quad (1.1)$$

Where A is Absorbance,  $P_{\lambda}^0$  is light emission power with wavelength of  $\lambda$ ,  $P_0$  is original emission power,  $\epsilon$  is molar absorptivity, c is sample concentration, l is distance travelled by the light in the sample.

#### 6.4.2 Molar adsorption coefficient

The Greek letter epsilon ( $\epsilon$ ) in the equation is called the molar absorptivity or the molar absorption coefficient. The larger the molar absorptivity, the more likely the electronic transition (*The Beer-Lambert Law*, 2017). For Plasticizers C and D, an  $\epsilon$  value of 25 was used (Kalliola *et al.*, 2015), but for the other two plasticizers, A and B it was determined using the equation 1.2.

$$\epsilon = \frac{A}{cl} \quad (1.2)$$

For this, a specific concentration of plasticizer was weighted and analyzed through UV-spectrophotometer. The specific molar absorptivity values are shown in Table 6. Different values can be found for molar absorptivity depending on the chemical formula that is absorbing the light. In plasticizer B, C and D the absorbance is caused by (aromatic) structures of lignin. In literature, different values can be found for them and they are dependent on the lignin type. Values of molar absorbances of different lignin types can be found from a book by Stephen Lin. (Lin and Dence, 1991) The absorptivity of plasticizer B was determined using equation 1.2. That was close to that presented for ligno-sulfonate (5.1.3.3) Plasticizer A was also determined analytically.

Table 6. Molar absorptivity values of plasticizers

Plasticizer	Molar absorptivity
A	20,0
B	10,7
C	25.0
D	25.0

#### 6.4.3 Molar mass by SEC

Size exclusion chromatography (SEC) is also known as gel filtration, gel permeation or molecular sieve chromatography. SEC has been a standard method for polymer fractionation and analysis of molecular weight distribution of polymers based on separation of polymer fractions with different molecular sizes, i.e., hydrodynamic volume. Integration of a light scattering instrument in the SEC system allows obtaining absolute molecular weights that do not rely on calibration with standards of known molecular mass. (Zhang *et al.*, 2015)

The molar mass measurements were performed by Size Exclusion Chromatography (SEC) using Waters HPLC in 0.1 M NaOH eluent and MCX 1000 and 100 000 Å columns (PPS Polymer Standards Service, Mainz, Germany) with ultraviolet (UV) detection at 280 nm. The number and weight average molar masses ( $M_n$ ,  $M_w$ ) and the molar mass distributions (MMD) were calculated relative to Na-polystyrene sulfonate standards (Na-PSS, 1600-267200 g/mol, American Polymer Standards Corporation, Mentor, OH, USA) with Empower 3 software. The water phases containing different amount of unadsorbed plasticizers were dissolved in analytical NaOH (0.1 M, Merck Titrisol, Darmstadt, Germany) to obtain a plasticizer solution of about 1 g/l. With the most dilute water phases, the proper concentration of 1 g/l could not be reached. The sample was filtered with 0.45  $\mu$ m PTFE membrane syringe filters. (VWR International, Radnor, PA, USA)

## 7 Results

### 7.1 Adsorption

All the samples were analyzed with a spectrophotometer. Background absorption was analyzed from a sample prepared without a plasticizer. The background absorption was subtracted from all samples and then using Lambert-Beer's law (Equation 1.1) the amount of unadsorbed plasticizer in water was calculated. This amount was then subtracted from the initial amount dosed resulting the amount of plasticizer adsorbed on the cement particle. Figure 8 shows the adsorption of each plasticizer on the cement as a function of the amount dosed on cement. All calculations can be seen in Appendix 2.

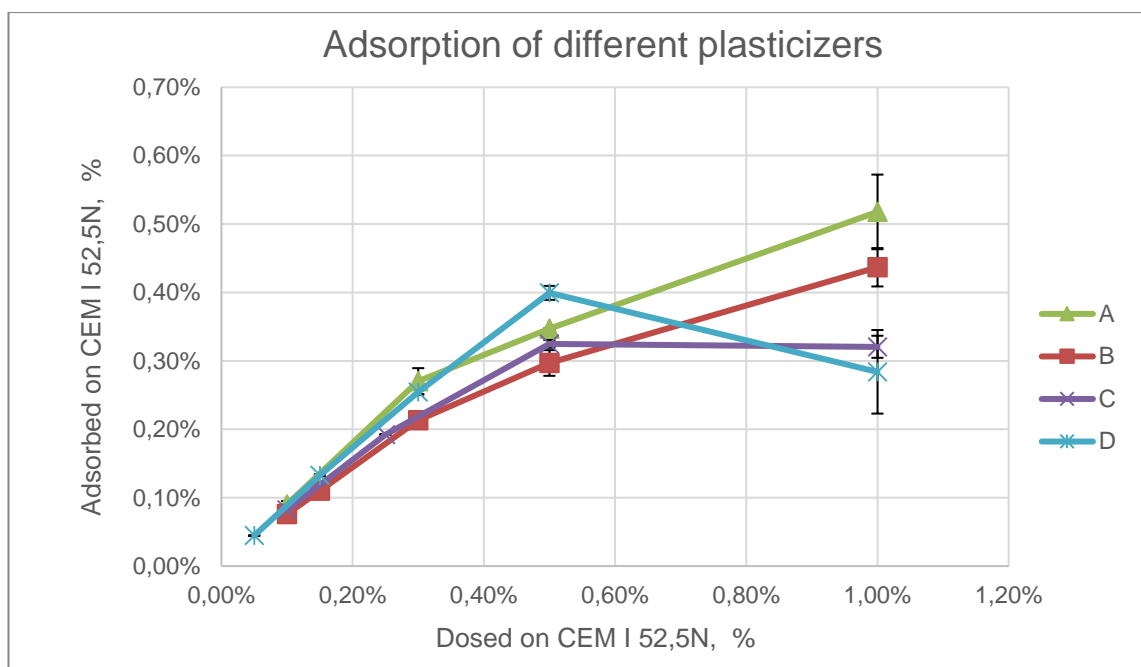


Figure 8. Plasticizer adsorption on cement and the standard deviations.

In the case of plasticizers A and B, the amount adsorbed was growing as a function of plasticizer dosing and did not found a maximum below dosage of 1,0 %. In the case of plasticizers C and D, the maximum adsorption was reached at dosage of 0.5 %.

## 7.2 Molar mass measurements

Figures 9-12 show the molar mass distributions (MMD) of the unadsorbed plasticizers at plasticizer dosing of 0,3(0,25)-1,0% on cement. MMDs of the unadsorbed material at the smallest doses (0,05-0,15%) are not included in the figures since the amounts in the water phase were lower than recommended for the SEC measurement. As a comparison for the distribution of the unadsorbed material, black line in figures shows the distribution measured from the plasticizer as such. Tables 7-10 show the corresponding weight ( $M_w$ ) and number ( $M_n$ ) average molar masses of the distributions and the polydispersity.

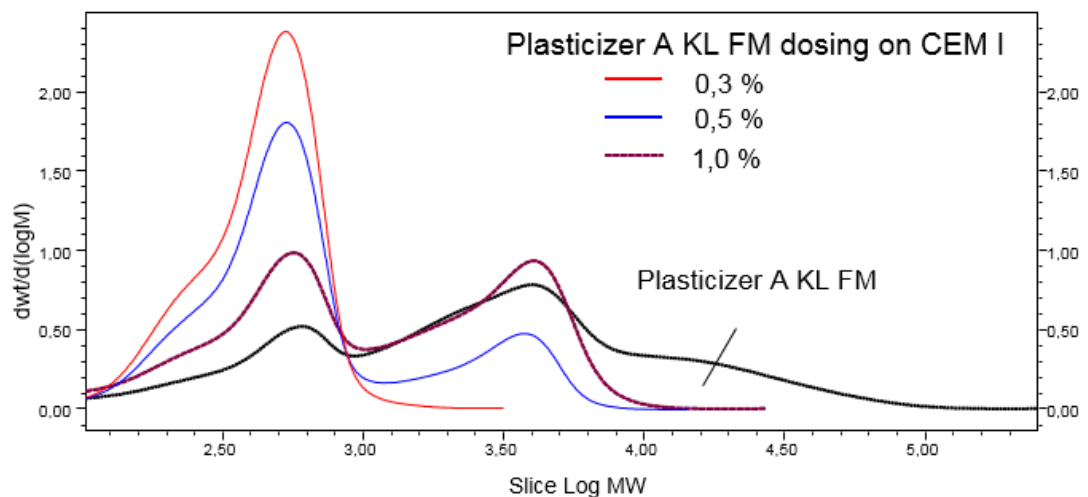


Figure 9. Molar mass distribution of the unadsorbed part of Plasticizer a found in the water phase at dosages 0,3-1%. Black line is showing the MMD of Plasticizer.

Table 7. Plasticizer A's molar mass Measured from the water phase as a formation of phasing

Dosed on CEM I, %	c(plast.) in supernat., g/l	$M_n$ , Da	$M_w$ , Da	Polydispersity
0	0,00			
0,1	0,13			
0,3	0,43	375	464	1,2
0,5	1,53	463	1058	2,3
1	4,44	654	1958	3,0
pure plasticizer		<b>1074</b>	<b>6762</b>	<b>6,3</b>

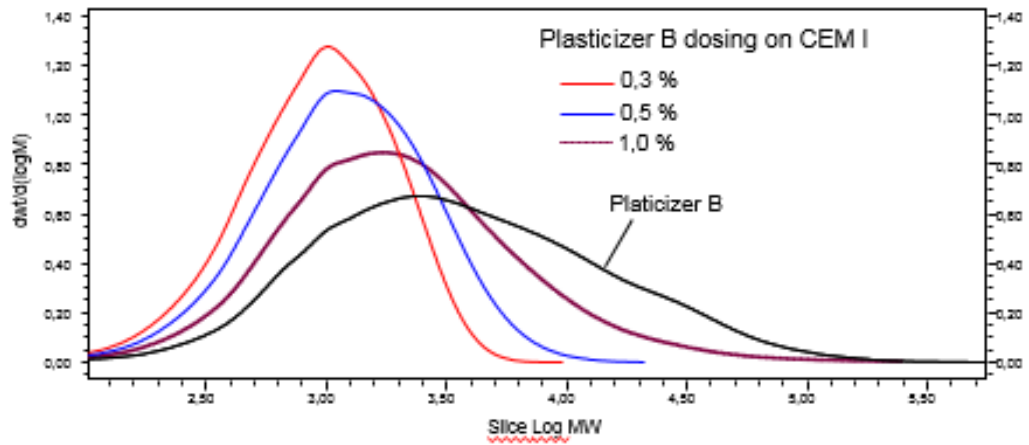


Figure 10. Molar mass distribution of the unadsorbed part of Plasticizer B found in the water phase at dosages 0,3-1%. Black line is showing the MMD of Plasticizer.

Table 8. Plasticizer B's molar mass Measured from the water phase as a formation of phasing

Dosed on CEM I, %	c(plast.) in supernat., g/l	Mn, Da	Mw, Da	Polydispersity
0,1	0,241	582	909	1,6
0,15	0,396	623	988	1,6
0,3	0,859	705	1181	1,7
0,5	1,972	851	1651	1,9
1,0	5,530	1164	4115	3,5
Pure plasticizer		<b>1677</b>	<b>9398</b>	<b>5,6</b>

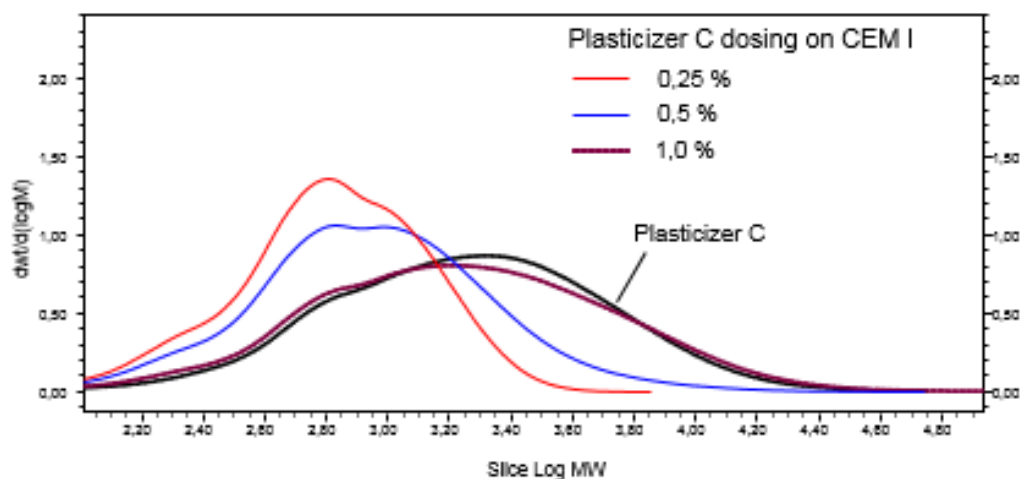


Figure 11. Molar mass distribution of the unadsorbed part of Plasticizer C found in the water phase at dosages 0,5-1%. Black line showing the MMD of Plasticizer.



Table 9. Plasticizer C's molar mass Measured from the water phase as a formation of phasing

Dosed on CEM I,%	c(plast.) in supernat., g/l	Mw, Da	Mw, Da	Polydispersity
0,1	0,18			
0,25	0,58	519	829	1,6
0,5	1,71	638	1374	2,2
1	6,68	1008	3094	3,1
Pure plasticizer		<b>1116</b>	<b>2982</b>	<b>2,7</b>

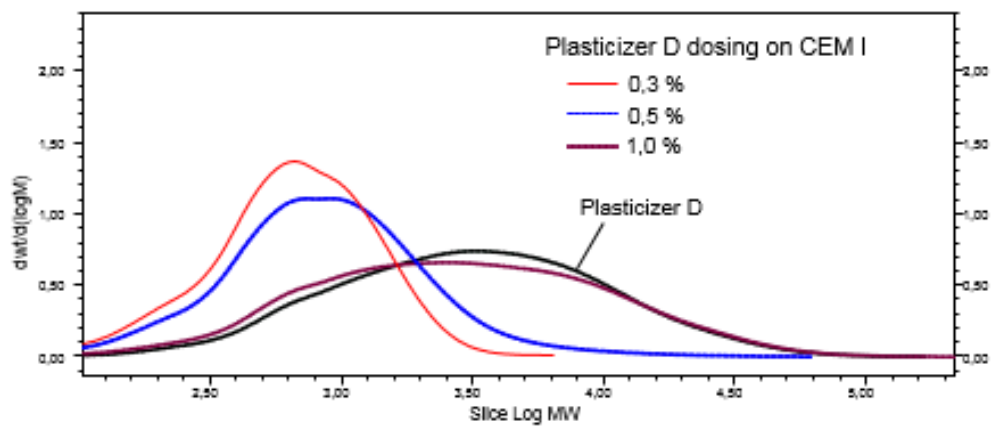


Figure 12. Molar mass distribution of the unadsorbed part of Plasticizer D found in the water phase at dosages 0,3-1%. Black line showing the MMD of Plasticizer.

Table 10. Plasticizer D's molar mass Measured from the water phase as a formation of phasing

Dosed on CEM I, %	c(plast.) in supernat., g/l	Mw, Da	Mw, Da	Polydispersity
0,05	0,06			
0,15	0,18			
0,3	0,48	520	819	1,6
0,5	1,08	626	1358	2,2
1	6,73	1354	6072	4,5
pure plasticizer		<b>1603</b>	<b>6152</b>	<b>3,8</b>

The results indicate that at 0.3 % dose the smaller-size molecules were not adsorbed on the cement particles, while the larger-size molecules were adsorbed entirely on the cement. With increasing dose of plasticizer, the MMD in the water phase was becoming more and more similar to that measured for the actual plasticizer product. At 1.0 % dose, the MMD of unadsorbed material was very similar to the actual plasticizer, indicating that the cement surface was fully covered or not more selectively absorbing the larger-size material. Adsorption behavior in terms of the plasticizer molar mass was measured to be very much alike for all the studied plasticizers.

### 7.3 Analyzing accuracy of the method

#### 7.3.1 Discrepancy in centrifuging

To analyze the difference centrifuge tubes, if they could be considered as one sample. This way the amount of analyzable sample could be increased and also save in the number of small sample tubes. Centrifuged paste samples were all separated into their separate containers. This separation was done to measure if the centrifuging process makes any difference for the three centrifuged parts. Standard deviations were calculated for the samples (see Table 11). Standard deviations were calculated from the adsorption percentage using the equation for the standard deviation (Equation 2).

$$\sqrt{\frac{\sum(x-\bar{x})^2}{n-1}}, \quad (2)$$

Where  $x$  takes on each value in the set, and  $\bar{x}$  is the average (statistical mean) of the set of values, and  $n$  is the number of values.

Table 11. Centrifuged sample deviations with one paste using plasticizer A (=SNF)

Plasticizer A sample	Dose	Adsorbed amount on CEM I, %				
		1	2	3	m(aver.)	stdev
1	<b>0.10 %</b>	0.08 %	0.08 %	0.08 %	0.08 %	0.000 %
2	<b>0.30 %</b>	0.23 %	0.22 %	0.23 %	0.23 %	0.002 %
3	<b>0.50 %</b>	0.21 %	0.21 %	0.22 %	0.22 %	0.003 %
4	<b>1.00 %</b>	0.36 %	0.35 %	0.35 %	0.35 %	0.007 %

The standard deviation of the centrifuged samples. show little variation. The variation is small: a maximum of 0,007 %. It is safe to assume that centrifuged samples had no significant differences in plasticizer concentration. After these tests, all centrifuged samples were pipetted in the same container.

7.3.2 Paste manufacturing and UV-spectrophotometry discrepancy

After finding that all the centrifuged samples could be considered the same, the testing method aimed to find whether the method was reliable. Five different concentrations were used to make five parallel paste samples. Doses of the samples can be seen Table 12. All of the parallel samples were analyzed twice (A and B) with UV-spectrophotometer (Figure 13). This experiment plan was to find the accuracy of the method and to differentiate how much discrepancy comes from the paste making and the spectrophotometer. Figure 13 shows the method for one dose. Table 12 shows the adsorption and deviations in each dose with each parallel sample.

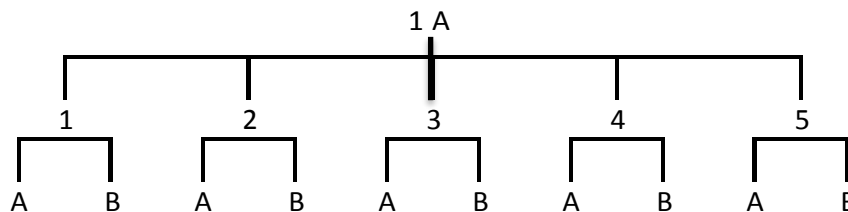


Figure 13. Method as a flow chart for one dose

Table 12. Deviations in samples. Five parallel and twice analyzed with UV-spectrophotometry

Plasticizer B	Dose	Adsorbed amount on CEM I, %						
		1	2	3	4	5	m(aver.)	stdev
1A	<b>0.10 %</b>	0.08 %	0.08 %	0.08 %	0.08 %	0.07 %	0.08 %	0.001 %
1B	<b>0.10 %</b>	0.08 %	0.08 %	0.08 %	0.08 %	0.07 %	0.08 %	0.001 %
2A	<b>0.15 %</b>	0.11 %	0.11 %	0.11 %	0.11 %	0.11 %	0.11 %	0.002 %
2B	<b>0.15 %</b>	0.11 %	0.11 %	0.11 %	0.11 %	0.11 %	0.11 %	0.002 %
3A	<b>0.30 %</b>	0.21 %	0.21 %	0.21 %	0.22 %	0.21 %	0.21 %	0.003 %
3B	<b>0.30 %</b>	0.21 %	0.21 %	0.21 %	0.22 %	0.22 %	0.22 %	0.004 %
4A	<b>0.50 %</b>	0.30 %	0.27 %	0.30 %	0.32 %	0.29 %	0.30 %	0.019 %
4B	<b>0.50 %</b>	0.31 %	0.29 %	0.30 %	0.33 %	0.31 %	0.31 %	0.012 %
5A	<b>1 %</b>	0.41 %	0.43 %	0.42 %	0.48 %	0.45 %	0.44 %	0.028 %
5B	<b>1 %</b>	0.46 %	0.44 %	0.45 %	0.48 %	0.45 %	0.46 %	0.016 %

The three samples of 1A, 2A, and 3A have almost no deviation between them. A drastic increase in deviations happens when using doses of 0.5 % and 1. %. The method becomes slightly more unreliable after a point where the increasing in the amount of plasticizer goes over 0.5 % when the plasticizer should be overdosed and remains unadsorbed on cement.

Then if we look at the discrepancy that comes from the spectrophotometer, it can be seen that the same happens with those results. After 0.5 %, the deviation starts to increase noticeably. Still, the deviation is not as significant as between the samples. The samples were analyzed only twice, which might affect the numbers a little. The total is the average deviation through all spectrophotometric analysis at a specific dosage. These numbers are so small that there should not be significant variability between spectrophotometric analysis. While doing the spectrums from the samples, it was found that the cuvettes can have a difference in absorptivity. Table 13 shows the deviation between the different scans of the spectrophotometer.

Table 13. Spectrum deviations

Sample	Dose	stdev					
		1	2	3	4	5	total
1AB	<b>0.10 %</b>	0,000 %	0,000 %	0,001 %	0,002 %	0,000 %	0,001 %
2AB	<b>0.15 %</b>	0,000 %	0,001 %	0,001 %	0,000 %	0,001 %	0,000 %
3AB	<b>0.30 %</b>	0,002 %	0,002 %	0,001 %	0,002 %	0,002 %	0,001 %
4AB	<b>0.50 %</b>	0,006 %	0,018 %	0,001 %	0,005 %	0,013 %	0,007 %
5AB	<b>1 %</b>	0,036 %	0,010 %	0,019 %	0,004 %	0,003 %	0,013 %

### 7.3.3 Langmuir isotherm

All plasticizer adsorption graphs seem to behave mostly like the Langmuir isotherm. With Equation 3 (Bey *et al.*, 2014) the theoretical Langmuir behavior can be calculated. This theoretical point and experimental points can then be studied to see if they correlate with each other.  $K_L$  and  $\Gamma_m$  need to be calculated first. The calculation was done using average plasticizer amount in water phase as a  $C_e$ .  $K_L$  and  $\Gamma_m$  were then approximated (computed) with Excel's solver function to find the smallest sum of differences between theoretical ad-sorbed plasticizers and experimental adsorbed plasticizers in all doses (Table 14). For plasticizer D the last data point was not included. (Bey *et al.*, 2014)

$$\Gamma = \frac{\Gamma_m K_L C_e}{1 + K_L C_e}, \quad (3)$$

Where  $\Gamma$  is amount adsorbed plasticizer per mass of cement (g/kg of cement),  $\Gamma_m$  is adsorption maximum,  $K_L$  is Langmuir's constant,  $C_e$  is Plasticizer concentration remaining in suspending fluid.

Table 14. Approximated adsorption maximums and Langmuir's constants

Plasticizer	$K_L$	$\Gamma_m$
A	6,46	1,72
B	2,18	1,67
C	7,41	1,03
D	4,57	2,07

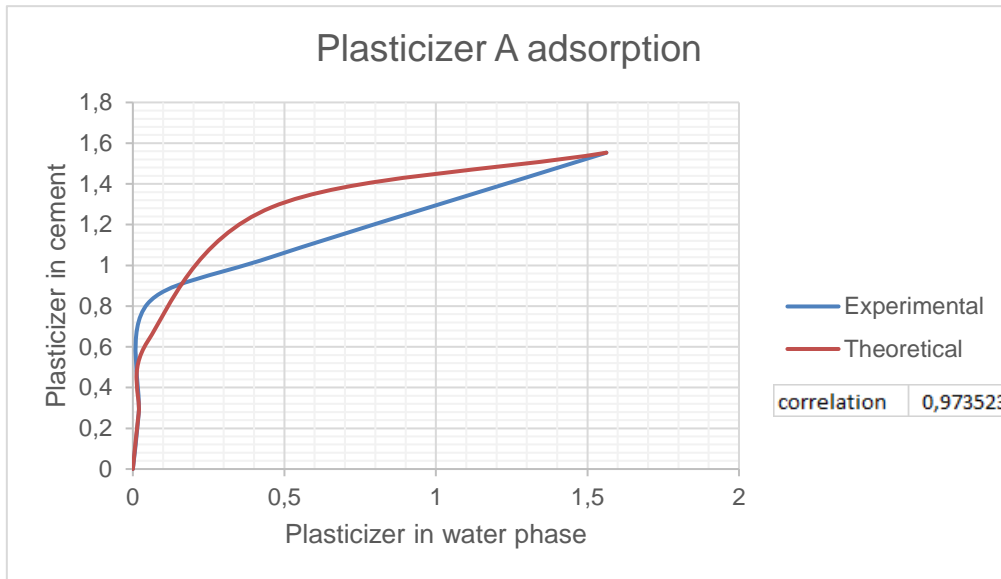


Figure 14. Plasticizer A Langmuir comparison: Experimental data vs. theoretical fitted curve.

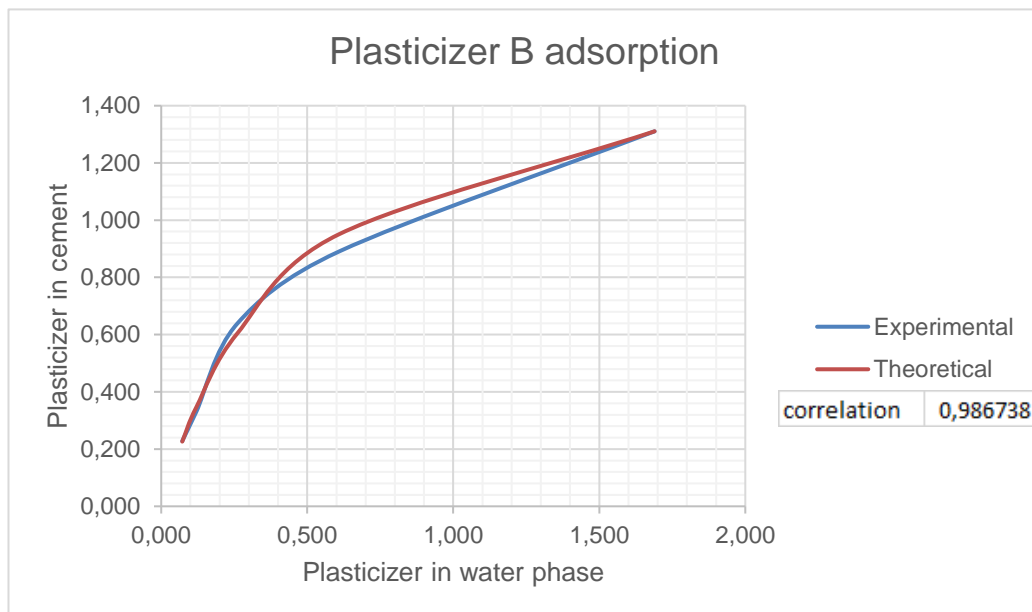


Figure 15. Plasticizer B Langmuir comparison: Experimental data vs. theoretical fitted curve.

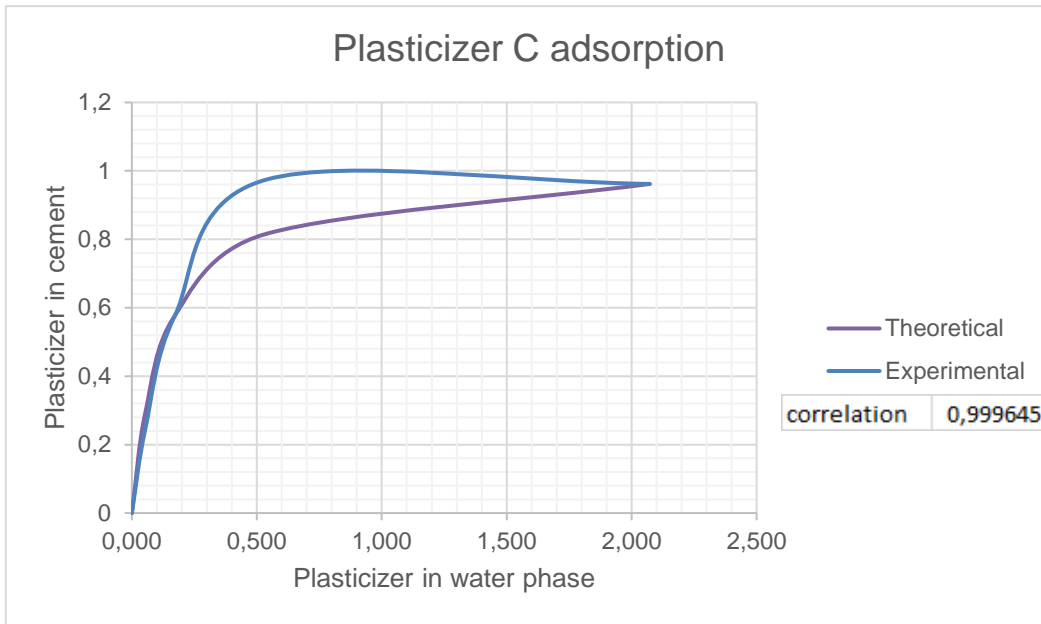


Figure 16. Plasticizer C Langmuir comparison: Experimental data vs. theoretical fitted curve.

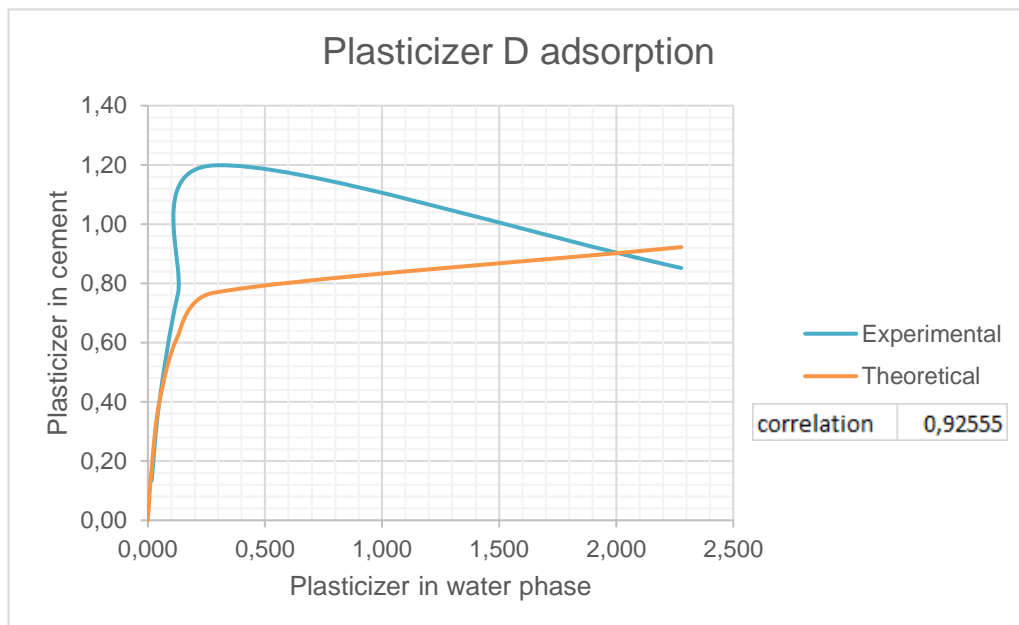


Figure 17. Plasticizer D Langmuir comparison: Experimental data vs. theoretical fitted curve.

Plasticizers A to D seem to correlate with fitted Langmuir isotherm. With this, all of them do behave like Langmuir. Plasticizer D has the lowest correlation of the plasticizer. This is due to the drop in adsorption that the curve shows. Langmuir cannot explain this. It is also to be noted that plasticizer B has many more data points than the other plasticizers.

## 8 Conclusions

When looking at the plasticizer behavior, the plasticizer mostly behaves like Langmuir. The correlations between the two were close. Only in case of the plasticizer D, it did lower significantly. If the last data point was not used in the calculation of the correlation, it would be over 0,99. With these calculations, it is safe to assume that the plasticizers behave like Langmuir isotherm.

The method used to analyze the four plasticizers is suitable to a point. In a typical range of plasticizer usage, the method is accurate and easy to perform. There were no significant differences between the analyzed paste samples also the fluctuation in UV-spectrophotometer was negligible. Overdosing a little did create more difference between the two samples, but not by significant amount. The method is usable, but massive overdosing might make the method unreliable.

After the point of where cement should not adsorb any plasticizer anymore, the extra should be found from the water phase. This point was not found with the plasticizers already in commercial use with the doses used. When more of the plasticizer did end up in the water phase; more did seem to end up adsorbed. This increase might be that it gets trapped somewhere in the process. More plasticizer is used in the manufacturing process to reduce the amount of water put in to keep the cement ratio. This increase makes the process of paste making harder since rinsing of the plasticizer comes harder, because of the decreasing amount of water used.

Size of the adsorbed molecules was consistent in all plasticizers. largest molecules were adsorbing first to the cement particles. This selective adsorption could be due to the higher anionic charge of the larger particles then, the smaller ones. With the more significant charge, they would be more inclined to find their way on the cement particle. This charge difference was not measured in this work. When more of the plasticizer was mixed with the cement, more larger particles could be found to not adsorb on the cement. The cement particle has limited space, and after the larger particles have covered most areas, only smaller ones would be able to go to the places that the larger ones left open.



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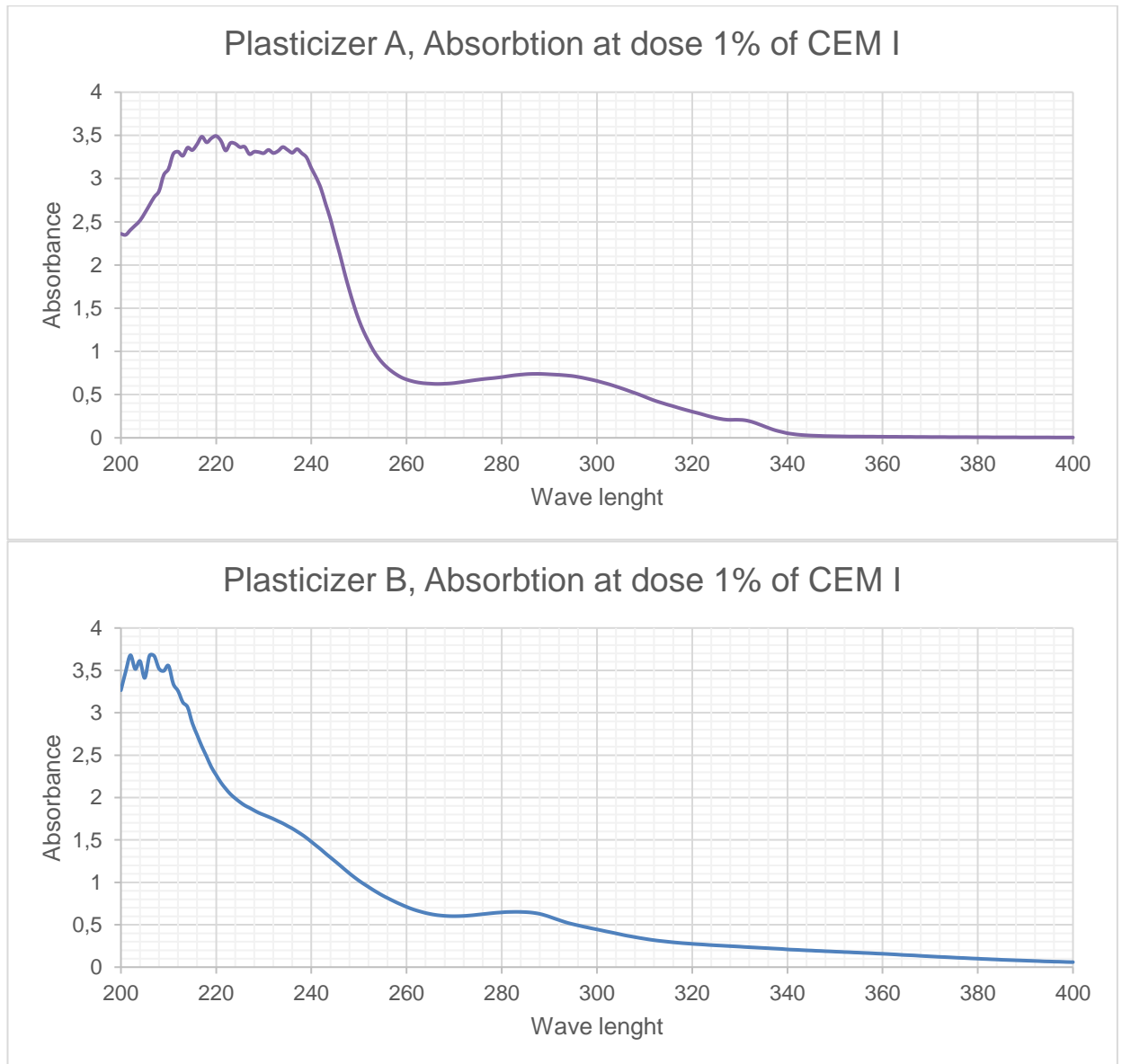
*The Beer-Lambert Law* (2017). Available at: [https://chem.libretexts.org/Core/Physical\\_and\\_Theoretical\\_Chemistry/Spectroscopy/Electronic\\_Spectroscopy/Electronic\\_Spectroscopy\\_Basics/The\\_Beer-Lambert\\_Law](https://chem.libretexts.org/Core/Physical_and_Theoretical_Chemistry/Spectroscopy/Electronic_Spectroscopy/Electronic_Spectroscopy_Basics/The_Beer-Lambert_Law).

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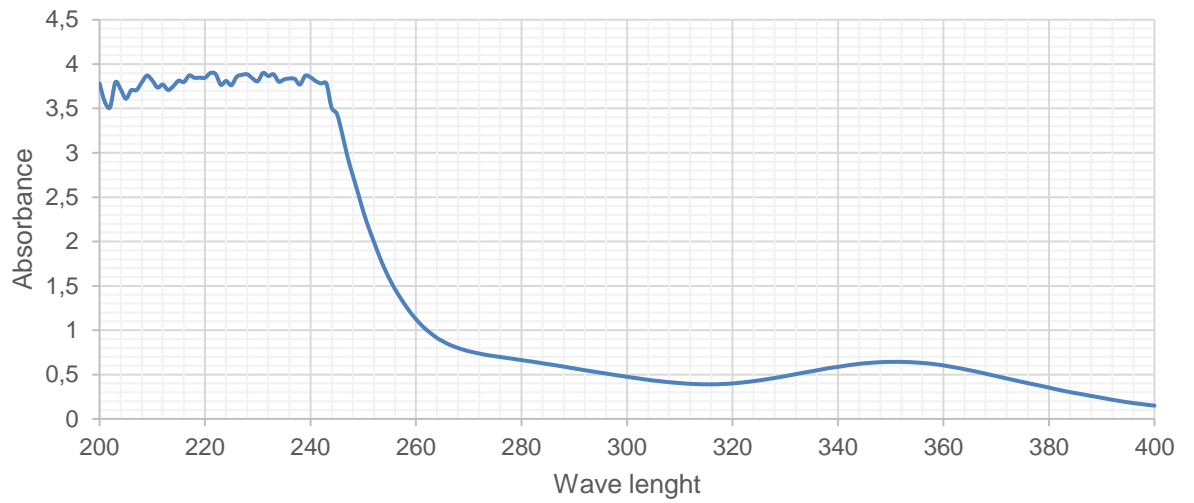
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## Appendix 1. Absorbance graphs for all plasticizers

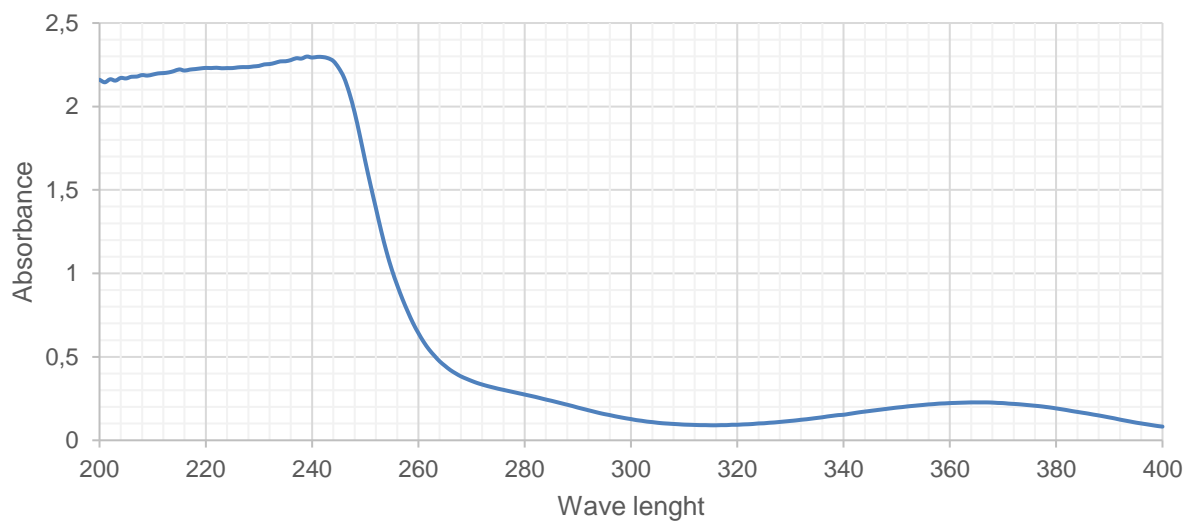
Absorbance graphs for all plasticizers with dose of 1% of the cements mass



Plasticizer C, Absorbtion at dose 1% of CEM I



Plasticizer D, Absorbtion at dose 1% of CEM I



## Appendix 2. Absorbance calculation tables

Tables to calculate the adsorbance in all plasticizers

Plasticizer	Dose, %	A2	A1	Wave length	Dilution factor	Absorptivity (a), g/(cm*l)	A1 sample	A2 sample	<b>A1 (sample- blank)</b>	<b>A2 (sample- blank)</b>	A(aver.) sample	c1, g/l	c2, g/l	
<b>Blank</b>														
	0	0	0,023	0,017	285	5	0,115	0,085			0,1			
<b>A</b>														
	1	<b>0,10 %</b>	0,547	0,276	275	5	20,026	2,735	1,38	<b>2,635</b>	<b>1,28</b>	2,0	0,132	0,064
	2	<b>0,30 %</b>	0,435	0,167	275	20	20,026	8,7	3,34	<b>8,6</b>	<b>3,24</b>	5,9	0,429	0,162
	3	<b>0,50 %</b>	0,615	0,613333	285	50	20,026	30,75	30,67	<b>30,65</b>	<b>30,567</b>	30,6	1,531	1,526
	4	<b>1 %</b>	0,593	0,696	287	150	20,026	88,95	104,4	<b>88,85</b>	<b>104,3</b>	96,6	4,437	5,208
<b>C</b>														
	5	<b>0,10 %</b>	0,462	0,46	280	10	25	4,62	4,6	<b>4,52</b>	<b>4,5</b>	4,5	0,181	0,180
	6	<b>0,25 %</b>	0,489	0,481	280	30	25	14,67	14,43	<b>14,57</b>	<b>14,33</b>	14,5	0,583	0,573
	7	<b>0,50 %</b>	0,429	0,449	280	100	25	42,9	44,9	<b>42,8</b>	<b>44,8</b>	43,8	1,712	1,792
	8	<b>1 %</b>	0,557	0,576	280	300	25	167,1	172,8	<b>167</b>	<b>172,7</b>	169,9	6,680	6,908
<b>D</b>														
	9	<b>0,05 %</b>	0,496	0,474	280	3	25	1,488	1,422	<b>1,388</b>	<b>1,322</b>	1,4	0,056	0,053
	10	<b>0,15 %</b>	0,472	0,417	280	10	25	4,72	4,17	<b>4,62</b>	<b>4,07</b>	4,3	0,185	0,163
	11	<b>0,30 %</b>	0,406	0,359	280	30	25	12,18	10,77	<b>12,08</b>	<b>10,67</b>	11,4	0,483	0,427
	12	<b>0,50 %</b>	0,541	0,469	280	50	25	27,05	23,45	<b>26,95</b>	<b>23,35</b>	25,2	1,078	0,934
	13	<b>1 %</b>	0,561	0,633	280	300	25	168,3	189,9	<b>168,2</b>	<b>189,8</b>	179,0	6,728	7,592

2 (4)

Plasticizer in water phase, g		Plasticizer in CEM I, g				Adsorbed amount of dosed, %				Adsorbed amount on CEM I, %			
m1	m2	m1	m2	m(aver.)	stdev	1	2	m(aver.)	stdev	1	2	m(aver.)	stdev
0,039	0,019	0,26	0,28	0,27	0,014	87 %	94 %	90 %	4,8 %	0,09 %	0,09 %	0,09 %	0,005 %
0,129	0,049	0,77	0,85	0,81	0,057	86 %	95 %	90 %	6,3 %	0,26 %	0,28 %	0,27 %	0,019 %
0,459	0,458	1,04	1,04	1,04	0,001	69 %	69 %	69 %	0,1 %	0,35 %	0,35 %	0,35 %	0,000 %
1,331	1,563	1,67	1,44	1,55	0,164	56 %	48 %	52 %	5,5 %	0,56 %	0,48 %	0,52 %	0,055 %
0,054	0,054	0,25	0,25	0,25	0,000	82 %	82 %	82 %	0,1 %	0,08 %	0,08 %	0,08 %	0,000 %
0,175	0,172	0,58	0,58	0,58	0,002	77 %	77 %	77 %	0,3 %	0,19 %	0,19 %	0,19 %	0,001 %
0,514	0,538	0,99	0,96	0,97	0,017	66 %	64 %	65 %	1,1 %	0,33 %	0,32 %	0,32 %	0,006 %
2,004	2,072	1,00	0,93	0,96	0,048	33 %	31 %	32 %	1,6 %	0,33 %	0,31 %	0,32 %	0,016 %
0,017	0,016	0,13	0,13	0,13	0,001	89 %	89 %	89 %	0,4 %	0,04 %	0,04 %	0,04 %	0,000 %
0,055	0,049	0,39	0,40	0,40	0,005	88 %	89 %	88 %	1,0 %	0,13 %	0,13 %	0,13 %	0,002 %
0,145	0,128	0,76	0,77	0,76	0,012	84 %	86 %	85 %	1,3 %	0,25 %	0,26 %	0,25 %	0,004 %
0,323	0,280	1,18	1,22	1,20	0,031	78 %	81 %	80 %	2,0 %	0,39 %	0,41 %	0,40 %	0,010 %
2,018	2,278	0,98	0,72	0,85	0,183	33 %	24 %	28 %	6,1 %	0,33 %	0,24 %	0,28 %	0,061 %

3 (4)

<b>B</b>	<b>Dose</b>	A1	A2	A3	A4	A5	Wave length	Dilution factor	Absorptivity (a), g/(cm*l)	A1 sample	A2 sample	A3 sample	A4 sample	A5 sample
14 I	<b>0,10 %</b>	0,265	0,274	0,261	0,25	0,288	287	10	20,026	2,65	2,74	2,61	2,5	2,88
14 II	<b>0,10 %</b>	0,269	0,269	0,246	0,276	0,287	287	10	20,026	2,69	2,69	2,46	2,76	2,87
15 I	<b>0,15 %</b>	0,428	0,483	0,432	0,428	0,426	287	10	20,026	4,28	4,83	4,32	4,28	4,26
15 II	<b>0,15 %</b>	0,422	0,47	0,422	0,432	0,412	287	10	20,026	4,22	4,7	4,22	4,32	4,12
16 I	<b>0,30 %</b>	0,328	0,323	0,317	0,296	0,31	287	30	20,026	9,84	9,69	9,51	8,88	9,3
16 II	<b>0,30 %</b>	0,316	0,313	0,32	0,287	0,301	287	30	20,026	9,48	9,39	9,6	8,61	9,03
17 I	<b>0,50 %</b>	0,212	0,251	0,215	0,196	0,222	287	100	20,026	21,2	25,1	21,5	19,6	22,2
17 II	<b>0,50 %</b>	0,203	0,223	0,216	0,189	0,202	287	100	20,026	20,3	22,3	21,6	18,9	20,2
18 I	<b>1 %</b>	0,638	0,616	0,623	0,561	0,592	287	100	20,026	63,8	61,6	62,3	56,1	59,2
18 II	<b>1 %</b>	0,584	0,601	0,594	0,555	0,587	287	100	20,026	58,4	60,1	59,4	55,5	58,7

<b>A1 (sample- blank)</b>	<b>A2 (sample- blank)</b>	<b>A3 (sample- blank)</b>	<b>A4 (sample- blank)</b>	<b>A5 (sample- blank)</b>	c1, g/l	c2, g/l	c3, g/l	c4, g/l	c5, g/l
<b>2,55</b>	<b>2,64</b>	<b>2,51</b>	<b>2,4</b>	<b>2,78</b>	0,237	0,246	0,234	0,223	0,259
<b>2,59</b>	<b>2,59</b>	<b>2,36</b>	<b>2,66</b>	<b>2,77</b>	0,241	0,241	0,220	0,248	0,258
<b>4,18</b>	<b>4,73</b>	<b>4,22</b>	<b>4,18</b>	<b>4,16</b>	0,389	0,440	0,393	0,389	0,387
<b>4,12</b>	<b>4,6</b>	<b>4,12</b>	<b>4,22</b>	<b>4,02</b>	0,384	0,428	0,384	0,393	0,374
<b>9,74</b>	<b>9,59</b>	<b>9,41</b>	<b>8,78</b>	<b>9,2</b>	0,907	0,893	0,876	0,817	0,856
<b>9,38</b>	<b>9,29</b>	<b>9,5</b>	<b>8,51</b>	<b>8,93</b>	0,873	0,865	0,884	0,792	0,831
<b>21,1</b>	<b>25</b>	<b>21,4</b>	<b>19,5</b>	<b>22,1</b>	1,964	2,327	1,992	1,815	2,057
<b>20,2</b>	<b>22,2</b>	<b>21,5</b>	<b>18,8</b>	<b>20,1</b>	1,880	2,066	2,001	1,750	1,871
<b>63,7</b>	<b>61,5</b>	<b>62,2</b>	<b>56</b>	<b>59,1</b>	5,929	5,725	5,790	5,213	5,501
<b>58,3</b>	<b>60</b>	<b>59,3</b>	<b>55,4</b>	<b>58,6</b>	5,427	5,585	5,520	5,157	5,455

4 (4)

Plasticizer in water phase, g					Plasticizer in CEM I, g							
m1	m2	m3	m4	m5	m1	m2	m3	m4	m5	m(aver.)	stdev	
0,071	0,074	0,070	0,067	0,078	0,23	0,23	0,23	0,23	0,22	0,228	0,004	
0,072	0,072	0,066	0,074	0,077	0,23	0,23	0,23	0,23	0,22	0,228	0,004	
0,117	0,132	0,118	0,117	0,116	0,33	0,32	0,33	0,33	0,33	0,330	0,007	
0,115	0,128	0,115	0,118	0,112	0,33	0,32	0,33	0,33	0,34	0,332	0,006	
0,272	0,268	0,263	0,245	0,257	0,63	0,63	0,64	0,65	0,64	0,639	0,010	
0,262	0,259	0,265	0,238	0,249	0,64	0,64	0,63	0,66	0,65	0,645	0,011	
0,589	0,698	0,598	0,545	0,617	0,91	0,80	0,90	0,96	0,88	0,891	0,056	
0,564	0,620	0,600	0,525	0,561	0,94	0,88	0,90	0,98	0,94	0,926	0,037	
1,779	1,717	1,737	1,564	1,650	1,22	1,28	1,26	1,44	1,35	1,311	0,084	
1,628	1,676	1,656	1,547	1,636	1,37	1,32	1,34	1,45	1,36	1,371	0,049	

Adsorbed amount on CEM I, %						
1	2	3	4	5	m(aver.)	stdev
0,08 %	0,08 %	0,08 %	0,08 %	0,07 %	0,08 %	0,001 %
0,08 %	0,08 %	0,08 %	0,08 %	0,07 %	0,08 %	0,001 %
0,11 %	0,11 %	0,11 %	0,11 %	0,11 %	0,11 %	0,002 %
0,11 %	0,11 %	0,11 %	0,11 %	0,11 %	0,11 %	0,002 %
0,21 %	0,21 %	0,21 %	0,22 %	0,21 %	0,21 %	0,003 %
0,21 %	0,21 %	0,21 %	0,22 %	0,22 %	0,22 %	0,004 %
0,30 %	0,27 %	0,30 %	0,32 %	0,29 %	0,30 %	0,019 %
0,31 %	0,29 %	0,30 %	0,33 %	0,31 %	0,31 %	0,012 %
0,41 %	0,43 %	0,42 %	0,48 %	0,45 %	0,44 %	0,028 %
0,46 %	0,44 %	0,45 %	0,48 %	0,45 %	0,46 %	0,016 %